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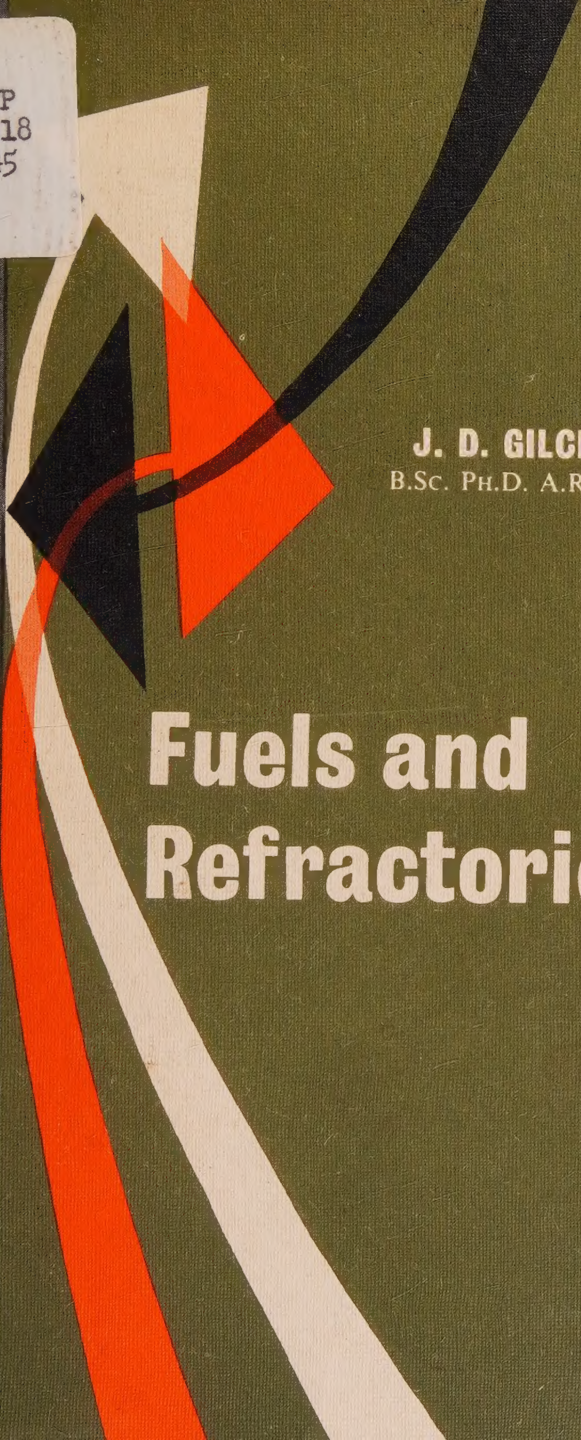

J. D. GILCHRIST
B.Sc. Ph.D. A.R.C.S.T.

Fuels and Refractories

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M. W. THRING, D. C. RHYS JONES, T. F. GASKELL

Fuels and Refractories

Fuels and Refractories

J. D. GILCHRIST
DEPARTMENT OF METALLURGY
KING'S COLLEGE, NEWCASTLE UPON TYNE
THE UNIVERSITY OF DURHAM

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Introduction

It is the purpose of this book to present a concise account of the ranges of fuels and refractory materials currently in industrial use and to discuss their characteristics and limitations in the light of modern practice. While each of these topics is interesting in itself the book is intended to be read as a preliminary to a study of furnace technology which is dealt with in a companion volume, *Furnaces*.

Fuels are the raw materials consumed by furnaces, the source of the energy which has to be converted into heat and put to a useful purpose raising temperatures or developing power. The amount of chemical energy available in any load of fuel is, of course, limited and is available only on one occasion so it is desirable that it should be put to the best use when that single opportunity is being exploited. Wasted fuel is a waste of natural resources. It is also a waste of money.

Electricity is not strictly a fuel but like the chemical energy of a fuel electrical energy can be converted to heat and used for raising furnace burden temperatures. For this reason the generation and distribution of electricity has been included for discussion almost as if it were another type of fuel like gas, coal, or oil. Brief consideration is given also to nuclear fuel—structural energy of whose atoms can be released as heat by fission under neutron bombardment.

Refractories are the heat-resisting materials from which furnaces are constructed. They are mainly bricks made from specially selected clays and other rocks blended, moulded to shape, and fired at high temperatures. These bricks are assembled on a steel or cast-iron framework to form the furnace, flues and other accessory parts which reach high temperatures. In many cases this brickwork is very durable and features as an almost permanent capital asset but deterioration with time is normal and in extreme cases, particularly, though not exclusively, in the metallurgical industries, conditions can be so severe that the useful life of refractory linings or roofs may be only a few weeks—indeed sometimes only a few hours. In these cases refractories are consumables and any better choice of brickwork or amelioration of conditions which will increase refractory life is of great value not only because the cost of refractories themselves is reduced but also because lost time required for rebuilding is also reduced. Intelligent choice of brickwork, like efficient use of fuel, can save a lot of money. It is customary to consider the cost of refractories per ton of product so that considerable increases in the price per brick can be absorbed if the more expensive brick lasts longer in the furnace, production rate being constant, or if it permits a higher production rate to be attained even though the brick life in hours is not increased.

These volumes are developments of lecture courses on furnace technology given to students of Metallurgy in King's College, Newcastle on Tyne (the University of Durham). The consequent bias toward metallurgical applications of fuel and refractories may be criticized by the reader whose interests lie elsewhere but the bias is not inappropriate in so far as the metallurgical industries have a wider experience of fuel technology than any others and most of the modern high quality refractories have been developed for or by the steel industry. The metallurgical industries are major users of fuel; they use all kinds of fuel and in the widest range of types of furnace including the largest built; they develop the highest temperatures and operate under some of the most arduous conditions, chemically and mechanically; their burning rates and flame intensities are among the highest used; and they can claim a large share of the credit for the advances in fuel technology which have taken place since the industrial revolution. These advances have included such classical "breakthroughs" as the invention of the hot blast stove in association with blast furnaces and the development of the regenerative principle on which the open hearth steel-making furnace depends. In more recent times the steel industry has done much to develop the use of oxygen (rather than air) for combustion of oil or gas—a phase of development which is not yet complete. Continuing demands for higher temperatures and faster production rates ensures that there is still plenty of scope for research and development and for the further improvement of combustion techniques.

Other industries are of course playing their own important parts in improving fuel utilization. An important example is the electricity industry whose new conventional generating plant operates at efficiencies undreamed of twenty years ago. The choice and availability of solid fuels have improved in recent years, mainly for the domestic consumer, while the design of domestic heating appliances has undergone a minor revolution. These improvements have the advantage that they often help the consumer to meet the requirements of the Clean Air Act but at the same time more efficient combustion and utilization of the energy produced tends either to lower fuel bills or to give greater comfort, amenity or production with the cost of the fuel unchanged.

No discussion about fuel can ignore economics. Fuel is used in almost every industry and its cost is often an important factor in determining the price of the product. A country which enjoys a plentiful supply of cheap indigenous energy should be at a considerable advantage when selling its manufactured goods in competition against other countries not so favoured, and indeed the established industrial areas of the world are, with a few exceptions, also major coal-producing areas.

The fuel bill of Great Britain is probably about £2000 million per annum or about 10 per cent of the national turnover. Obviously it is in the interest of both the individual and the nation to get the best possible value for this money. The individual may exploit the current advantages in price or in technology to be gained from the use of one fuel rather than another at any particular time and governments not infrequently influence individuals in their decisions by the application of taxes or subsidies. Ultimately, however, value for money is best assured by organizing for the highest possible efficiency of utilization of fuel at all points in the economy—not only by the steelworks and power-stations but also by humbler users right down to shops, offices and homes, for homes use more fuel in Britain than the steel industry, and it is in the shops, offices and homes that the efficiency is at present lowest and the potential saving greatest. Unfortunately it is usually necessary to make a substantial capital outlay in order to convert to efficient equipment, and it is not always apparent that money will in fact be saved in the change-over. There is probably a good case for subsidizing such conversions. There is certainly a case for prohibiting by law the installation of new equipment which does not utilize its fuel with an efficiency which is well up to the best that is currently possible.

PART ONE

Fuel

1. Classification of Fuels

Omitting consideration of electrical energy until Chapter 8, fuels can be classified in several different ways.

Most fuels are "fossil fuels", that is coal, or oil, or their derivatives. The few exceptions are important only for very restricted purposes. They include, for example, metallic aluminium in the "thermit" process, and sulphur in some roasting operations. There are many metal extraction processes where the heat of reactions contributes a high proportion of the energy requirements as in the conversion of iron to steel by the Bessemer or other pneumatic processes, where the fuel may be said to be silicon, carbon and phosphorus. Another non-fossil fuel is wood with its derivative, charcoal. Peat and lignite are included among the coals but peat especially is on the borderline between "vegetable" and "fossil". Wood, charcoal and peat are not used in large quantities by industry today but they are not obsolete. Reserves of peat are large and it is used in at least one place for generating electricity. Charcoal too is still used in small iron blast-furnaces in countries where wood is more plentiful than coal, or where special metallurgical requirements have to be satisfied. Vegetable waste like spent sugar cane, and sewage gas provide useful local supplies of energy in undeveloped and in highly industrial regions respectively.

Fuels may be classified as raw, or prepared. Thus we have raw coal and crude oil on the one hand, and on the other, prepared or refined products like coke, refined oils and pitches. The proportion of raw fuel used is decreasing. Coal would seldom be used unwashed and ungraded, and burning appliances are now designed to accept particular sizes of coal or coke. Cokes and prepared fuels like "Coalite" are becoming more necessary as atmospheric pollution is more and more discouraged, but again good design of burning appliances can extend the use of raw coal. Metallurgically, coke is the most important derivative of coal, but several kinds of gas are also prepared and used in vast quantities.

Oil is seldom used crude, but is usually refined by fractional distillation and other processes, different fractions being put to different purposes. The lightest fraction of all—natural gas—is often available at the oilfield in very large quantities. Where circumstances permit, this gas is piped to industrial areas. It can also be liquefied and transported in tankers over great distances. It is the heavy fractions which are most often used in metallurgical industries, often so heavy that they have to be warmed to permit pumping through pipes. Even the residual pitch is available as a fuel.

Fuels may be solid, liquid or gaseous, as already implied. Liquid and gaseous fuels can more conveniently be handled in pipelines than solid fuels. They can be more or less on tap, whereas coal and coke must usually be moved in batches. To this there are exceptions, however. Lump coal can be taken long distances within a plant on conveyor belts and can be fed to furnaces on moving grates and pulverized coal can be blown with air along pipes. On the other hand, oil, while readily handled in hydraulic systems, is usually delivered by tanker in batches, and pipeline distribution is as yet only between major oil storage installations. Solid fuel is most readily stored, in the open if necessary, though not without some difficulties being encountered. Oil and gas must be held in closed containers, each of limited, if large capacity and the bleeding to waste of unwanted excess by-product gas is sometimes an unfortunate necessity. The use of old gas wells or similar suitable strata for storing gas and possibly oil too has been suggested and might afford a useful buffer against seasonal variation in demand.

Fuels are sometimes referred to as being rich or lean. This refers to the available calories per unit of mass or volume. Coke with 90 per cent of carbon is richer than say peat which has a high water content. Natural gas is richer than say producer gas which has a high nitrogen content.

2. Properties and Tests

These can be dealt with here only in a general way since different fuels have peculiar properties and special tests which can best be discussed separately at later stages. The flashpoint of an oil, for example, has no counterpart in solid fuels but all fuels have a calorific value and a chemical composition and it is this latter type of property which will be discussed here.

Chemical Composition

Fossil fuels and their products are composed of mixtures of organic compounds of carbon, hydrogen, oxygen, nitrogen, sulphur, etc., along with some inorganic matter which is identified in the residual ash after combustion.

The carbon and hydrogen are of greatest importance as heat producers, other elements being at best diluents. Oxygen, for example, would usually be combined with hydrogen or carbon in compounds which would have to be endothermally dissociated during combustion, so reducing the effective heating effect of the carbon and hydrogen.

The organic compounds in coal are very complex, usually called humic acids and with molecular weights of several thousands. The oils contain a wide range of hydro-carbons—paraffins, olefines, naphthalenes and aromatics—ranging from the simplest compounds like methane (CH_4) up to waxes of very large molecular weight. Normally these are separated according to volatility before being marketed, each fraction for a particular purpose.

Sulphur is an important impurity in both coal and oil fuels. In coal it is partly mineral and partly organic, being present at about 1 per cent in British coals, but it may be much higher in some seams. The mineral part is largely FeS_2 which is visible in seams and veins but too finely disseminated to be economically separated. In oil it is wholly organic and in this form it cannot possibly be eliminated completely from the fuel. The proportion of sulphur in oil is also about 1 per cent, but may be lower, or higher up to about 3 per cent, when the fuel becomes metallurgically unsuitable. Low sulphur fuel is in great demand as it reduces the amount of metallurgical work necessary particularly in steelmaking.

Nitrogen is present in coal at between 1 and 2 per cent and in crude oil at under 0·5 per cent. Oxygen also is very low in oil but in coal it may rise to about 20 per cent and even higher in lignite, being an essential part of the coal substance.

The free moisture content particularly of solid fuels is important to know, when buying, when using or when analysing. Coals and cokes have a large internal area due to their finely porous structure and therefore adsorb moisture from the atmosphere. This leads to an inherent moisture content dependent on the humidity. A much higher value is frequently encountered due to rain, washing (of coal) or quenching (of coke), and it should be kept to a minimum by storage and handling practice.

Inorganic matter, determined as ash after total combustion of coal in air, is probably mainly mineral in origin, though some is very closely associated with the coal substance or so finely disseminated as to be physically inseparable from it. A part of the ash will probably come from "dirt" bands and from the shale bands overlying and underlying the coal seam, but most of this should be separated by washing. The ash content of coals may be between about 1 and 15 per cent, but the range 5–8 per cent is probably typical for British coals. The ash is mainly silica, alumina and ferric oxide with varying amounts of other oxides such as CaO, MgO and Na_2O. This is not, of course, the condition of the inorganic matter in the coal, and the decomposition and conversion of clays, shales, carbonates and sulphides into oxides or even into alumino-silicates, involves some change in weight, usually a loss. In coke, on the other hand, the original minerals have already been decomposed and probably reduced, and ash may be heavier than the inorganic content of the fuel due to the oxidation, particularly, of iron.

The ash content of heavy oil is only about 1 per cent, and it is less in light oils and greater in pitch, in which it concentrates in the fractionation processes. This ash is rather different from coal ash in that it may be rich in sodium sulphate and vanadate, the latter derived from the remains of fossilized fish. This is of consequence when the high-temperature corrosive properties of these substances are likely to be effective, especially in internal combustion engines and gas turbines.

The fusion point of ash is also important and varies from about 1050°–1500°C. In Britain more than half the seams yield coals whose ash fusion point exceeds 1200°C and these include the best coking coals. Of the remainder only a very few have fusion points below 1100°C. This fusion temperature determines the form in which the ash is most likely to be removed from the furnace—as a dry ash, as a clinker, or even as a slag—and this obviously has an important bearing on details of furnace design. Generally, if the fusion point exceeds 1200°C clinkering may occur but does not often give trouble. Ash is, however, likely to be non-homogeneous and clinker can be formed by the cementing together of quite refractory pieces of ash with relatively small amounts of fusible material, particularly if high in iron oxide. Much of the ash of pulverized coal is carried off as "fly-ash" in the chimney gases, but if it is fusible it can gradually build up on the walls of the furnace chamber or in the flues. Fly-ash, if produced in large quantities, as for example by large electricity generating plants, may have to be precipitated out of the chimney gases before discharge to avoid offence to the public.

The chemical composition of a fuel determines the amount of air required to burn it. For the carbon content:

$$C + O_2 = CO_2$$

Thus every 12 g carbon require 32 g oxygen or 22·4 l. (at N.T.P.). Similarly, for the hydrogen content:

$$2H_2 + O_2 = 2H_2O$$

For every 4 g of hydrogen, or 44·8 l., 32 g oxygen, or 22·4 l. are required.

Any oxygen already present in the fuel is available toward these reactions. The remaining oxygen requirement must be supplied, normally as air with a composition 21 per cent O_2 : 79 per cent N_2 by volume or 23·2 per cent : 76·8 per cent by weight. If oxygen enrichment is employed these natural ratios must of course be modified.

Gas analyses are usually in terms of volume percentages of the various components—H_2, CO, CH_4, CO_2, N_2, etc. In this case the oxygen and hence the air requirement for complete combustion is calculated in a similar manner:

$$2CO + O_2 = 2CO_2$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Two volumes of CO require one of oxygen but one of methane requires two of oxygen, and so on.

The ultimate analyses of *solid fuels*, that is for all elements present, are determined by methods generally adopted in organic chemistry. Carbon and hydrogen are determined together by combustion to CO_2 and H_2O which are absorbed and weighed. Nitrogen is converted to ammonium salts under sulphuric acid with a selenium catalyst in the Kjeldahl method, the ammonia then being distilled off and determined by colorimetric or volumetric means. Sulphur is determined by combustion to sulphate either in an oxidizing fusion or by O_2 in a bomb, converted to $BaSO_4$ and weighed. Ash analysis is conducted separately by standard inorganic methods (as for ores and slags). Care has to be taken to make due allowance for moisture content (at the time of weighing out the sample) and the distinction has often to be made between organic sulphur and that part which appears in the ash.

For day-to-day control "proximate" analysis is usually sufficient. In coal this involves standard tests for moisture, volatile matter, fixed carbon, ash and sulphur. The volatile matter is determined by heating a dry sample out of contact with air at 925°C. Loss of weight is "Volatile Matter" (V.M.) and the residual weight is "Fixed Carbon" + "Ash". Ash alone is determined in a separate sample by total ignition in air at 800°C and hence fixed carbon is calculated as the difference. The fusion point of the ash, if required, is determined by comparison with Seger cones as in the refractories test on bricks.

Oil fuels undergo a variety of analytical tests, which vary with the kind of oil and the uses to which it is to be put.[1] *Specific gravity* may be required for conversions of volumes to weights or to meet specifications, and would be of interest when oils were being mixed or blended. *Viscosity* is of interest when heavy oils have to be pumped through supply lines and it may be necessary to have data over a range of temperatures. *Flash point* is an "ignitability test" and provides information about handling dangers on the one hand, and ease of lighting up on the other. *Distillation tests* indicate what fraction or blend of the oil one is handling. Taken together these tests go far to define the "type" of oil, in terms light, medium and heavy.

Moisture may be determined in oils by settling out or centrifuging if in large amounts or by a standard distillation method. It is most likely to be present in the heavy fractions. *Sulphur* is determined by burning the oil sample in special apparatus in which the products of combustion can be drawn through an absorbent solution (Na_2CO_3) and the acidity due to SO_3 measured volumetrically, or, in the case of heavy oils, by oxidation with oxygen in a bomb and determination as sulphate. *Ash* is determined by evaporation of most of the oil followed by ignition of carbonaceous residues. Other special purpose tests distinguish aromatics from paraffins and measure carbon residues and asphaltenes which are undesirable in engine fuels but of little consequence in furnace fuels.

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[1] The Institute of Petroleum *Standards for Petroleum and its Products*, Vol. 1.

Gaseous fuels are analysed by molecular species present, the results being expressed in percentages by volume. A convenient volume of gas is isolated (at a temperature and pressure which must be kept constant). It is then brought into contact with a series of reagents which absorb the constituents one at a time, the volume lost at each stage being noted. CO_2 is absorbed by KOH; O_2 by alkaline pyrogallol; and CO by ammoniacal cuprous chloride. Unsaturated hydro-carbons can be absorbed by fuming H_2SO_4. Hydrogen and methane and other saturated hydro-carbons cannot be absorbed in this way, and must be oxidized to H_2O (which condenses) and CO_2. There are several ways of doing this. Explosion with an excess of oxygen is a common method but slow combustion methods have some advantages. Oxidation by a heated CuO spiral converts only CO and H_2 to CO_2 and H_2O, leaving CH_4, C_2H_6, etc., unaffected. This can be followed by combustion on a platinum (catalyst) spiral when the quantities of CO_2 and H_2O formed will indicate the proportions of CH_4 and C_2H_6 in the gas. Obviously an accurate gas analysis is not easy, and complete separation not always possible in a single series of operations. SO_2, H_2S and HCN go with CO_2 while C_2H_2 will be absorbed along with CO unless special extra steps are incorporated.

Calorific Value

Chemical composition determines the calorific value (c.v.) of a fuel. This is the amount of heat obtainable by complete combustion of unit quantity of fuel. Unfortunately, it can be expressed in several different ways and it is often necessary to convert from one system to another.

The unit of heat is, for scientific purposes, most conveniently the *calorie*, or gramme calorie, being the amount of heat required to raise the temperature of 1 g of water from 15° to 16°C. The British Thermal Unit (B.t.u.) is more frequently used in industry, and is the amount of heat required to raise the temperature of 1 lb of water from 60° to 61°F. There is a further Centigrade Heat Unit (C.H.U.) which compromises between the other two and is the heat required to raise the temperature of 1 lb of water by 1°C.

The unit quantity of fuel should then be the gramme or the pound but gaseous fuels are usually measured by volume so we get B.t.u. per lb.; B.t.u. per cubic foot; C.H.U. per cubic foot; calories per gramme, and so on. Metric units will be used here, but frequent conversions will be necessary when comparing data in the other books (see Table 1).

Table 1

Conversion Factors

1 gramme calorie (cal)	=	0·001	kg cal. (kcal.) (cal.)
	=	0·002205	Centigrade Heat Units (C.H.U.)
	=	0·00397	British Thermal Units (B.t.u.)
	=	0·000001163	Kilowatt Hours (kWh)
	=	4·186	Joules = Watt–seconds
	=	4·186 × 10^7	ergs
1 cal per g	=	1	kcal per kg
	=	1	C.H.U. per lb
	=	0·556	B.t.u. per lb
1 kcal per m^3	=	1000	cal per m^3
	=	0·0625	C.H.U. per ft^3
	=	0·1122	B.t.u. per ft^3

A distinction must be drawn between *Gross* and *Net Calorific Value.* When hydrogen is present in a fuel, water vapour is one of the products of combustion, and if this is condensed the latent heat liberated may be added to the other heats of combustion, to give the Gross Calorific Value of the fuel. Indeed the temperature to which the condenser in the test equipment is cooled is specified at 60°F (in Britain). In many practical cases, however, the combustion gases are not condensed in the working part of a furnace and the Net Calorific Value of the fuel, i.e. omitting the part available from water vapour between 100° and 60°C, is of greater interest. Obviously the difference is often very small and quite unimportant (unless costing is being based upon it), but in those cases where hydrogen or methane is a major constituent the difference is large and it is important to use the value appropriate to the purpose in hand.

In principle, calorific values can be calculated from complete analyses, if all the heats of reactions occurring during combustion are known. Certain assumptions have to be made, notably that combustion is complete to CO_2 and H_2O. This can be arranged in laboratory test equipment but often does not happen in a working furnace. Dissociation of compounds present in the fuel should also be taken into account and this is often very difficult as the compounds involved are many and complex. Usually formulae used to convert analyses into calorific values are empirical, and based on measurements on similar fuels using calorimeters.

Calculation of calorific value is most successful in the case of gaseous fuels where compounds are relatively simple and their net heats of combustion are usually known. Accuracy depends only on that of the gas analysis.

$$\begin{aligned}
H_2 + \tfrac{1}{2}O_2 &= H_2O & \Delta H &= -55{,}809 \text{ calories (net)} \\
CH_4 + 2O_2 &= CO_2 + 2H_2O & \Delta H &= -191{,}782 \text{ calories (net)} \\
CO + \tfrac{1}{2}O_2 &= CO_2 & \Delta H &= -67{,}623 \text{ calories}
\end{aligned}$$

To calculate the c.v. of a mixture, the analysis should be converted to gramme-molecular volumes, and the appropriate proportions of the gramme-molecular heats of the reaction added together and the sum related to unit volume of gas.

Direct determination of c.v. by calorimeter is carried out in standardized equipment. Solids and liquids are probably best determined using a bomb calorimeter in which the sample is ignited in an excess of oxygen contained in a small pressure vessel immersed in a water bath insulated from its surroundings. The rise in temperature of the water bath is measured and the heat produced by the reaction calculated via the thermal capacity of the apparatus.

Gas calorimetry involves burning gas at a constant rate, and transferring the heat from the gases produced into a counter-flowing stream of water via a suitable heat exchanger.

Calorimetry usually gives gross c.v. but the Boys' gas calorimeter collects the condensed water for measurement to enable the conversion to be made accurately to net c.v.

3. Coal

Origins

Coal is certainly derived from wood and other vegetable matter, decomposed first by bacteria under anaerobic conditions such as are still to be seen in some tropical swamps, and later modified by temperature and pressure.

Although coal-like substances can be produced from cellulose and resins in the laboratory, the exact conditions under which coal was formed are not known, nor are the variations in conditions which led to the variety of coals which are found. Factors which might be relevant are the degree of de-aeration in the early stages, the pH in the early stages, temperature and pressure in later stages and the time during which each stage persisted. The nature of the original vegetable matter may also have been important, particularly where segregation of parts like spores and cuticles by water flow may have occurred. Some coals have been modified by heat treatment due to their proximity to igneous intrusions.

Coals occur in seams which vary in thickness from a few inches to several feet. In the major coal-fields there are many such seams separated by thicker beds of shales, clays, sandstones and other sedimentary rocks. These series of strata may be faulted or folded, but across any coal-field the properties of the coal from any particular geological horizon are substantially constant while the quality varies more or less regularly from one seam to another in the vertical direction. For some purposes, notably carbonization, it is very desirable that the coal shall be drawn from a particular seam, and the exhaustion of such a seam would lead to temporary difficulties for the user until a new source of a similar coal could be found.

Coal can be won from seams down to 18 inches thick by conventional deep-mining methods if the quality is high enough and conditions favourable. Most coal is deep-mined but open-cast mining opportunities exist in most coal-fields and this can be the more economical process if the overburden does not exceed about a hundred feet. Out-cropping seams may be altered by weathering near the surface but in general open-cast coal is similar in quality to deep-mined coal from the same seam.

Classification

There are a number of classification systems for coals—not all compatible with one another.

TABLE 2

Typical Analytical Data for the Range of Coals, and Coke

Fuel	Ultimate—dry ash free basis			Proximate—air dry basis			Air dry C.V. (net) cal/g.
	%C	%H	%O	% Moisture	% V.M.	% Ash	
Peat	60	6	34	20	70/60	1/10	3500
Lignite	70	8	22	15	50/40	8/12	5000
Sub-bituminous coal	75/82	6/5	20/12	10	40/30	5/10	5500
Bituminous coal	82/90	6/4·5	12/3	2	35/20	5	7750
Semi-anthracites	91/93	4	4	1	10	5	8000
Anthracite	94	3	2	1	8	3	8000
Coke	95	1	2	2	8	7	7300

A rough preliminary grouping is given in Table 2. Peat and lignite are of no metallurgical importance, but where available in quantity they are dried and used industrially. Peat is used for the generation of electricity in Eire and lignites for gas production and domestic purposes, the largest user being Germany. Anthracite is a scarce and expensive high-grade fuel used industrially for steam raising and central heating. It is virtually smokeless, which makes it useful in malting. It is also used metallurgically as a carburizing agent and deoxidizing agent. The important range of coals is the bituminous group which merges into the anthracites at about 90 per cent carbon. These can be further classified in a manner which suggests the uses to which they might be put, as shown in Table 3.

TABLE 3

Typical Compositions of Some Bituminous Coals

	Carbon %	Hydrogen %	Oxygen %	V.M. %
Long flame, non-caking steam and house coals	83/86	5/6	6/12	30/40
Long flame, partly caking gas coals	82/86	4·5/5·5	5/9	30/40
Short flame coking coals	85/89	4·5/5·5	4/7·5	20/30

Industrially, this classification is of great importance, particularly in the separation of coking and non-coking types. Obviously classification by carbon content or "rank" is important in separating coals of very different characteristics. The use of volatile matter content, which is roughly complementary to rank, would divide up coals in a similar way. Within these divisions, however, there may be further sub-divisions and even an overlapping of these from one main division to another, so that the scheme is never so clear-cut as suggested above. Important factors other than carbon content include oxygen and hydrogen content and the ratio between them. This probably reflects the nature of the original organic matter and in turn affects the coking and caking properties. The Seyler classification attempts to cover all these factors. A simpler diagrammatic representation is presented in Fig. 1 which broadly indicates how quality is related to composition.

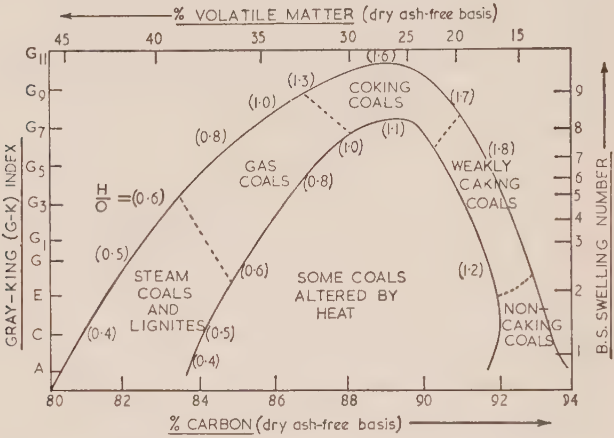

FIG. 1. A summary of the relationships between rank, volatile matter content, hydrogen : oxygen ratio, and coking characteristics of coals. The numbers in brackets are the H/O ratios at the upper and lower edges of the band which contains most normal coals. At any given rank, in general, a high proportion of hydrogen to oxygen favours strong swelling and agglutination.

Four types of coal substance can be recognized visually. *Vitrain* is bright, black and brittle and usually in thin bands. It fractures conchoidally. It contains no obvious plant structure and seems to have been derived from bark. *Clarain* is not so bright and has an irregular fracture. It contains more plant remains (spores, etc.) than vitrain and is the commonest of the four types of coal substance. *Durain* is duller, greyer and very hard, and cracks irregularly. It is highly charged with durable plant remains (spores, cuticle, etc.), and it is thought that durain was formed from silts or muds of small particles of vegetable matter. Cannel coal may be an extreme form of durain. It is associated with a high clay content and in extreme cases may become a sort of shale. *Fusain*, a soft powdery form occurring only in thin seams between bands of the other types, seems to have been formed differently from them. Massive coal fractures through fusain bands. About half of a coal seam may be clarain, a sixth to a third durain. Vitrain may rise to 10 or 15 per cent, while fusain is only present up to 1 or 2 per cent.

In coal preparation, durain and clarain may segregate as "hards" and "brights" respectively. While in any seam the analyses and characteristics of hards and brights are of the same order, there would usually be some small difference in properties, particularly in so far as the brights, vitrain and clarain, would have rather greater coking power.

A system of microconstituents in coal has been suggested, the important ones being the hydrogen-rich exinite, derived from spores and cuticles, fusinite which is relatively low in hydrogen, and vitrinite of intermediate hydrogen content. Clarain and durain are mixtures of these. Seyler found ten varieties of vitrinite whose reflectivities varied in geometric progression. In any coal only three or four of these are found, one predominating and this is determined by the rank of the coal.

Coals are sometimes examined by solvent extraction techniques which demonstrate the differences between coals but do not explain them.

Heating to release gas and tar is embodied in other empirical tests of interest to the carbonizing industry, which is also interested in the quality of the coke residue. The best known test on this group is the Gray–King assay in which 20 g of sample is heated in a silica tube to 600°C and the coal visually classified A to G by comparison with standard photographs depending on whether the residue remains a powder (A), or coalesces into a hard coherent mass with the same volume as initially (G). Intermediate stage B is non-caking, C and D are weakly caking while E, F and G are medium caking. Strongly caking coals swell and are designated G_1, G_2, etc., to G_{10}, the suffix indicating the number of grammes of inert carbon which must be blended into the 20 g charge to give zero swelling. The G–K index correlates well with rank and volatile matter and is probably the best index of the caking capacity of a coal or coal blend. Another common test gives as an index the British Standard Swelling Number, 1–9. A sample of coal is heated at a standard rate in a crucible with a lid on until volatiles cease to be evolved and again the shape and size of the button are compared with standard charts. The relationships between the agglutinating properties of a coal or coal blend and rank, volatile matter content and hydrogen/oxygen ratio are summarized in Fig. 1. A simple diagram of this kind is rather approximate and ignores many exceptional cases and must not be used to predict the behaviour of any individual sample.

Preparation

"Run of mine" coal is a mixture of all sizes from 2 or 3 ft across down to dust, along with shale from the floor and roof and dirt bands from within the seam. The coal will be veined with pyrites and other minerals and may even comprise different kinds and qualities of coal. In thick seams these different coals may be separated to some degree at the coal face.

Cleaning the coal is the removal as far as is practicable of the shale, dirt and veined minerals. Apart from this the coal may be prepared for use by separating the different types present, by breaking if necessary to smaller sizes and by screening to standard size ranges. Run of mine coal would probably be sized to ±3 or 4 in. The large coal would be cleaned by hand-picking and sold for domestic or railway use, or broken to smaller sizes. The undersize would be cleaned by "washing" which would be a gravity separation of coal from shale in equipment similar to those used in ore dressing. Jigs are the commonest type used for coal but riffle tables are also used, and flotation for fine coal. Dry methods—air suspension—are also used occasionally. Coal must be "de-watered" after washing, usually by a draining process.

Breaking is in either pick or roll-type breakers, which should be operated to crack the lumps rather than crush them, to minimize production of fines.

Sizing is by static or vibratory screens or trommels, to standard size ranges known in the trade by particular names:

Large cobbles	– 6 in.	+ 3 in.
Cobbles	– 4 in.	+ 2 in.
Trebles	– 3 in.	+ 2 in.
Doubles	– 2 in.	+ 1 in.
Singles	– 1 in.	+ ½ in.
Peas	– ½ in.	+ ¼ in.
Grains	– ¼ in.	+ ⅛ in.

The sizes are for round apertures, and the efficiency of screening is specified in terms of the proportion of allowable undersize. Large coal and slack are specified as over or under stated sizes.

The "natural" size distribution from a mine or an area depends on type of coal and mining methods, and is unlikely to be the same as the demand size distribution. Breaking always produces fines so that there may be times when it is not easy to market the whole of production. If fines are in excess, briquetting may be adopted to use them up.

An increasing proportion of coal is pulverized, usually in air-swept ball mills, to sizes about – 100 mesh (mostly much less). This uses up fines and even necessitates breaking down large coal as the demand increases. The main application of pulverized fuel is in power stations and other steam-raising plant. Almost any coal could be used. It need not be clean but it should be dry. Weakly caking steam coal is most suitable. Pulverizing is usually carried out on the site of the furnace or boiler from suitably small material, but pipe-line transport within a works area is quite practicable.

Storage

The storage of coal is not as simple as it might appear. There is a danger of spontaneous combustion due to heat generated by atmospheric oxidation. This danger is greatest in freshly mined coal and is usually serious only in large dumps of over 200 tons. The danger is reduced by restricting the height of the stack to 8 ft, by ensuring very adequate ventilation or by stifling it altogether with dust and by water spraying if necessary.

There is also some deterioration during storage over extended periods due to oxidation. There is some loss of calorific value, some reduction in size and an increase in friability. The coking quality may also be impaired. This deterioration is least with large coal. It increases with temperature. It can be mitigated by careful stacking designed to minimize ingress of air.

Uses

The utilization of coal in Britain is presented diagrammatically in Fig. 4. Gas works and electricity stations absorb about 38 per cent of the annual production between them, much of it high-grade coal, although the modern generating stations can use low-grade coal pulverized. Shops, offices and homes use another 25 per cent for space heating and domestic purposes, plus their share of gas and electricity. Most of this goes on open fires and into small boilers producing steam for central heating. When collieries and railways have been supplied, only about 30 per cent or 60 million tons a year (in 1960) are left for industry. The iron and steel industry uses about half of this either directly or through its carbonization plants. Heavy chemicals use coal as a raw material as well as a fuel, requiring about 6 million tons per annum for these purposes so that the rest of industry uses only about 25 million tons out of nearly 200 million.

The raw coal used by these general manufacturing industries is probably applied mainly to steam-raising, the steam being used for a multitude of heating and power-raising purposes. In the modern boiler plant the coal is fed mechanically on to moving grates which also clear themselves of ash. This kind of plant demands well-sized, well-washed coal but is easy to operate and much more flexible in operation and better controlled than the old hand-fired boilers. The more efficient combustion which results also gives a much cleaner discharge from the chimney. Coal can still be seen occasionally in older plants, firing reverberatory melting furnaces, or reheating furnaces in forges or in brickmaking kilns, but for most of these and similar purposes its use is now obsolescent. Oil and gas firing are more flexible and cleaner. Pulverized coal is often used, however, in small rotary melting furnaces, in billet reheating furnaces, and other hearth furnaces. The fly-ash produced tends to build up inside the furnace and can be a nuisance, but in well-designed furnaces control and flexibility are good and a long heating flame is readily obtained.

4. Carbonization

Carbonization of coal is its decomposition by heat, out of contact with air, into a solid residue, coke, and liquid and gaseous distillation products.

Types of Process

While the products of carbonization are always coke, gas and liquor, the main objective of the process is usually the production of either hard coke or gas, the liquor being a valuable by-product in each case. The carbonizing industries are then the gas industry and the coke industry, with a small but growing "smokeless fuel" industry taking at present a poor third place.

If gas is the primary objective, coal is used which has a high volatile content and moderate caking power though a coherent coke must be produced. If hard coke is being produced the coal required must have good coking power, found in coals of high rank (88–91 per cent C) and medium volatile matter content (25–30 per cent) (dry ash-free basis).

Coals are usually blended, that is strongly coking coals are mixed with weakly coking ones or with non-coking material like coal breeze or fusain dust. This helps to conserve the rather scarce strongly coking varieties, produces more gas than these varieties would do alone, and is indeed necessary under the fast coking conditions employed today, which would produce very coarsely porous coke if the "best" coking coal was carbonized without dilution.

As coking coal is heated through a narrow temperature range at about 300°C it becomes plastic or even fluid and at this stage most of the decomposition occurs. Gas and tar are evolved and bubbles form in this plastic mass. As the temperature rises further the residue solidifies again and freezes-in the porous macrostructure. Further heating continues to drive off volatile matter and the fine structure develops an increasing degree of order toward that of graphite.

In the process about half the sulphur distils off as H_2S and the remainder is fixed mainly as FeS. Oxygen and hydrogen are largely eliminated and half the nitrogen escapes as NH_3 and C_2N_2.

Carbonizing for gas is carried out in retorts or ovens and may be continuous or static. In the discontinuous process large moulded fireclay or silica retorts are used 20 ft long by about 2 ft across and with a round or ⌓-section. These are mounted horizontally in batteries and are heated by producer-gas burned with recuperator preheated air. Flue temperatures may reach about 1300°C but the charge will not all be so high. Each retort holds about a ton of coal which will carbonize in about 12 hr. The coke is pushed through with a ram and water quenched. Volatiles are taken off each retort via an ascension pipe connected at the door on one end and led to a collecting main and thence to condensation and gas-cleaning plant.

Continuous processes are usually conducted in narrow vertical chambers, the walls of which are heated by gas burning in the surrounding flues. Coal is fed at the top and coke withdrawn at the bottom at a rate which determines production rate, and, of course, the form of the heating cycle and hence the coke quality. Steam may be passed through the charge (cf. gas producer, p. 40), to cool the coke and bring about a higher degree of gasification. There are numerous designs of equipment but the principle involved does not change. Gas coke is made in ovens in a similar way to "hard" coke (see under) but from a different coal blend and using a rather lower temperature.

Metallurgical coke or "hard" coke was traditionally made in beehive coke-ovens and a little is still made this way. The product was very large-sized and highly unreactive. The simple beehive was slow, inefficient and had no facility for collecting the by-products. Its evolution eventually permitted by-products to be collected and thermal efficiency improved especially when the ovens were arranged in batteries, but the modern oven is much more efficient, productive and easy to work. It gives higher yields and lends itself better to the use of inferior coking coals. The coke produced is usually smaller in size but even this is probably more appropriate to modern needs. The modern coke-oven is a vertical chamber about 12 ft high, 40 ft long and 14–22 in. wide, with a capacity for about 12–20 tons of coke which is produced in about 10–20 hr.

The oven walls are of silica brick, the high-temperature strength of which ensures a very long life and enables the walls to be built thin for a high rate of heat transference through them.

Ovens are arranged in batteries, each pair being separated by a system of vertical flues in which the fuel gas is burned. Producer gas, blast-furnace gas or coke-oven gas may be used. Air for combustion (and the gas too if lean) is preheated in regenerator chambers beneath the ovens. The temperature in the flues has to be about 1350°C.

There are a number of different oven designs (Otto, Becker, Koppers, Simon–Carves, etc.), which differ mainly in the arrangement of the flues. The main aim is to produce a uniform temperature over all the oven walls in the battery, and the operation of the battery is also directed toward this end. Ovens are charged and discharged in a special order to preserve this uniform distribution of temperature and avoid damage to the battery through a badly distributed load, especially if the coal swells.

The ends of the ovens are sealed with heavy brick-lined doors which are handled by service vehicles which run on each side of the battery. Ovens are charged by a multiple-hopper charging vehicle which runs across the top of the battery and pours the blended coal, hammer-milled to $-\frac{1}{8}$ in., through a series of ports in the oven roof. During coking, gas and tars are taken off via an ascension pipe and passed into the gas-collecting main. Coke, when fully carbonized, is pushed by a ram out of the oven into a quenching car and quenched with water. Proper quenching leaves just enough heat in the coke to dry out the residual water. An alternative "dry quenching" uses circulating gas ($N_2 + CO$) which transfers the heat to waste-heat boilers; damage to coke is said to be reduced, but maintenance costs are high and the system is not popular.

During carbonization coal swells at first but shrinks as the temperature rises. This can put some pressure on the walls and it is important that an oven should not be pushed until the coke has shrunk clear of the walls. It is also important to blend the charge so that it will eventually do so.

As carbonization proceeds the temperature in the coal rises gradually from the wall inwards, and a narrow zone of plastic coal at about 300°C advances slowly from each wall toward the centre. Behind it there is coke and ahead there is coal. The gas and tar go forward to the middle, then up and out, probably leaving some of the tar behind.

Ultimately, the zones meet at the centre which is now only at about 300°C although the outside is at 1300°C. Some time must be allowed for the centre too to graphitize, but the outside and inside coke are never quite the same.

The two large sheets of coke in the oven are fissured in a honeycomb pattern, and on discharge break into pieces roughly half as long as the oven is wide and about 6–10 in. across. The outer (cauliflower) ends are hard, silvery grey and finely porous. The inner ends are often softer, almost black, and the pores are more obvious. There may be further variations in appearance, hardness and reactivity with position in the oven, particularly from top to bottom as affected by the mode of charging. The properties of a coke depend mainly on the nature of the coal (blend) but also on operating conditions. The most strongly coking coals (e.g. Durham) give the most unreactive cokes, while the weakly coking coals (e.g. Midlands) produce relatively reactive cokes. Any given coal will yield a more unreactive coke if carbonized slowly, for example, in a wide 22-in. oven, than if coked in, say, a narrow, fast-working continuous vertical retort. High temperatures and long times at temperature also reduce reactivity but induce cracking and may reduce the size of the coke. Coal moisture content, coal size and method of charging also affect the properties, probably by way of their effects on heat transfer through the charge.

Modern practice favours a medium width of oven to effect a compromise between the rather small, but hard and uniform coke from the narrow oven and the higher output of possibly less reactive lumpy coke of the wide oven.

Carbonization, however, remains to some extent an art and a skilful operator, given a reasonable choice of coals and not too hard pressed for output, can usually produce good-quality coke.

Low-temperature carbonization is primarily aimed at the production of smokeless domestic fuels such as "Coalite" or "Furnacite". The temperature used is only 500°–600°C and low heat transfer rates at so low a temperature are countered by the use of very thin layers, by stirring or by internal heating of the coal charge by producer gas or superheated steam. The fuel produced is reactive, smokeless and suitably sized for domestic use. The yield of gas is low, but a high yield of a tar is obtained which is particularly suitable for adaptation to liquid fuel and is a valuable source of aromatic by-products. This part of the carbonizing industry has become much more important and is still expanding, and much research is being done on finding ways of producing smokeless fuels from a much wider range of coals so that they can be made available in almost any part of the country without incurring high transport costs.

Products and Yields

Table 4 gives typical proportions of the various products of coal carbonization in gas-works and in metallurgical coke-oven practices. The major differences between the two are due to the types of coal treated—high and low volatile coals respectively.

TABLE 4

Typical Yields of the Various Products of Carbonization of Gas Coal in Retorts and Coking Coal in Coke Ovens

Product	Gas Retort (weight %)	Coke Oven (weight %)
Coke	65	75
Gas	22	14
Tar	4	3
Benzole	1	1
Ammonia	1	1
Water	6	5

For any given coal blend, however, there may still be considerable variation in yields due to operating conditions, particularly temperature and duration of coking, and heating rates. The operation of the by-products plant will also affect these figures as the items listed are not sharply defined. The lighter paraffins, for example, may be divided in varying proportions between gas and tar.

The primary separation of the by-products is carried out in several stages:

1. Cooling of the gas, for condensation of tar and ammoniacal liquors.
2. Electrostatic separation of remaining tar.
3. Reheating of gas and washing with sulphuric acid for conversion of ammonia to ammonium sulphate. At this stage the ammonia from the liquors (1) are reintroduced to the system and also sulphated.
4. Gas is oil washed to remove benzole.

5. Further oil washing for naphthalene.
6. Desulphurization with iron oxide.
7. Drying with calcium chloride or glycerine to reduce the dew point.

It will be obvious that this amounts to a gas-cleaning operation and all stages are necessary if the gas is to be sold for general distribution. Gas for internal use may not go through stages 5, 6 and 7. The removal of sulphur would usually appear to be advantageous in metallurgical works but is not always carried out for economic reasons.

While by-product recovery is economically desirable it is also a practical necessity if the gas is to be recovered clean. The overall economic picture is complex and changes from time to time. At one time ammonium sulphate was an important credit, but it can now be produced more cheaply by other means and probably barely pays for its removal. At present benzole production is more profitable. The tar is further treated by distillation to the technical fractions naphtha, light oils, carbolic oil, creosote oil, anthracene oil and pitch. The exact fractionation applied depends on demand. Further splitting up of these fractions for rarer or more valuable aromatic compounds is not likely to be undertaken at the coke- or gas-works.

The properties of the gas produced is discussed in Chapter 6.

5. Coke

Classification

There is a clear distinction between gas coke and metallurgical or "hard" coke. The former is smaller, weaker and more reactive. Its chemical composition is not closely specified and its pore structure is likely to be rather open. It is well suited for domestic appliances for which it should be closely sized and as free as possible from inclusions of shale which cause it to spark. It can also be used in small central heating plant and in gas producers.

Hard coke is made primarily for the metallurgical industries and particularly for foundries, for use in cupolas and crucible melting furnaces and for blast furnaces. The traditional beehive coke was very large and unreactive and afforded a means of attaining very high temperatures. Modern coke is smaller and perhaps rather less unreactive, but meets present-day requirements well.

On leaving the ovens, coke is quenched with water, dried and then screened. The smaller sizes (below about 2 in.) are sold for domestic and general purposes, and only larger sizes used in blast furnace or foundry. Obviously the yield of large-sized coke should be high at this stage and further breakdown prior to use should be as small as possible. "Domestic" coke, down to about $\frac{1}{4}$ in., is less valuable than "blast-furnace" coke. Breeze, below $\frac{1}{4}$ in., is not easy to get rid of in large quantities.

Properties and Tests

The relevant properties of coke will be discussed under the following headings:

1. *Chemical*
   - (a) Analytical — Proximate—H_2O, S, ash, volatile matter and fixed carbon.
     Ultimate—C, H, N, O and ash analysis.
   - (b) Reactivity — to CO_2 and O_2.
   - (c) Calorific value

2. *Physical*
   - (a) Strength — Shatter tests, Drum tests, Size analysis.
   - (b) Analytical — Real density, Apparent density, Bulk density, Porosity.

All of these properties may be examined in either gas coke or hard coke, but the discussion which follows concerns mainly the properties of hard coke as required in iron-making as it is here that the highest quality is required and testing is carried out most rigorously.

1. *Chemical Tests*

The effects of chemical analysis on the metallurgical process are largely calculable. *Moisture* should be down to below 3 per cent. It must not be paid for and charged to the furnace as carbon. *Sulphur* in coke becomes part of the metallurgical load, entering metal and slag. In iron-making 90 per cent of the sulphur comes from the coke, and much of it must be removed as CaS necessitating an addition of limestone and a corresponding amount of coke to heat and melt it. The sulphur content of coke is usually about 1 per cent. It should be as low as possible but users often prefer a steady value even if it is always higher than the minimum occasionally attainable. Similarly *ash*, which is present at about 10 per cent, should be low, but steady. Ash is largely silica and alumina and must be fluxed in the blast furnace with lime which in turn must be heated and melted. *Volatile matter* is not available as fuel and should be low (1 per cent), especially as this would indicate thorough coking. *Fixed carbon* is used for estimating the calorific value of the fuel and should be about 85 per cent or more if the ash is low.

The *ultimate analysis* is seldom carried out as a routine, because it is tedious and gives information which probably doesn't change much from day to day and tells little more than the proximate analysis. Typical values on a dry, ash-free basis would be:

	%
Carbon	95
Hydrogen	1
Nitrogen	1
Sulphur	1
Oxygen	2

It should be understood that most of the sulphur will be as FeS—the Fe appearing in the ash analysis.

The determination of *reactivity* (to CO_2) and that of *combustibility* (to O_2) are usually research jobs. The only standard test is the "Critical Air Blast" (C.A.B.) test which is a test of "ignitability". This is carried out by determining the minimum air flow rate through a bed of fuel, which will maintain its combustion once started. Less official tests involve comparing the rate of weight loss of standard samples of fuels under standard conditions, in atmospheres of air, oxygen, or CO_2. The results obtained depend very much on the conditions under which these tests are carried out—such as the temperature, pressure and gas flow rate—and the reaction rate alters during the test.

Any distinction between reactivity and combustibility is probably false since those factors which affect one will always affect the other in a similar way. There is, however, a hope among users that a coke which is extremely unreactive to CO_2, but extremely combustible in air, will be developed. This seems most unlikely ever to happen.

Reactivity depends on the carbonization conditions—mainly temperature and time—on the pore structure of the coke to some extent and probably on the nature and amount of minor impurities in the material which can exercise a catalytic effect. The reactivity of very pure char is known to be very low, but it is increased by even small additions of iron or sodium oxide (among other things) probably according to mechanisms such as:

$$\begin{aligned} 2Fe + O_2 &= 2FeO \\ 2FeO + 2C &= 2Fe + 2CO \end{aligned}$$

and

$$\begin{aligned} Na_2O + CO_2 &= Na_2CO_3 \\ Na_2CO_3 + C &= Na_2O + 2CO \end{aligned}$$

Coke is sometimes sprayed with sodium carbonate solution to enhance its reactivity for domestic use.

The *calorific value* of coke is rather lower than that of anthracite or even of bituminous coals. This is partly because of the lower hydrogen content and also because of the higher ash content (see Table 2).

2. *Physical Tests*

Coke strength is usually measured by subjecting a sample of large coke to standardized abuse and sizing the products on standard screens. Occasional reports have been made of tests designed to measure the strength or hardness of the coke substance rather than that of the coke lumps—hardness and abrasion tests. These might be of significance in research but cannot describe the initial tendency of coke to break down to small sizes as this is very dependent on the system of cracks which develops in the oven or during cooling.

The Shatter Test was for long the standard test in Britain. Fifty pounds of + 2 in. coke were dropped four times from 6 ft on to an iron plate and sized on 2 in., 1½ in., 1 in., and ½ in. square-mesh screens. This test was originally developed to show the probable size distribution on arrival in the blast furnace in a typical works, presuming the sample to be representative of the coke on entering the works at coke-oven screens or railway sidings.

Good metallurgical coke (e.g. South Wales and Durham) would give a size analysis after shattering something like 80, 90, 96, and 98 per cent, while a poor coke (Yorkshire) would give 65, 80, 90 and 95 per cent. If the – ½ in. fraction in the Yorkshire coke fell to 3 per cent, this coke would be considered remarkably good, but if in a Durham coke it rose to 3 per cent it would be considered poor. In fact, it is the day-to-day variations that are important *within* a coke plant rather than the comparison with incomparable plants, and these day-to-day variations can be considerable, depending on coal blend, oven temperatures, carbonizing time and other factors. Users prefer regular quality.

Attention tends to be focused on the + 1½ in. and – ½ in. figures and the latter is often said to be the most important for blast-furnace operation as such small coke is most unwelcome in the furnace. Small sizes are screened out before charging but if the coke is weak more may form within the furnace.

The alternative *Micum Trommel Test* was imported from Europe about 1945. In this 50 kg of large coke + 50 mm was rotated in a drum, with internal lifting shelves, for 100 revolutions in 4 min and then sized on round-holed screens at 100, 80, 40, 20 and 10 mm diameter, the oversize in each of these being quoted. Attention was paid mainly to the + 40 mm and - 10 mm fractions. This test often fails to agree with the Shatter test in its assessment of coke strength. Abrasion is taken more into account by it but the main difference is that it tests the coke after a much greater degree of abuse than does the Shatter test—in fact to the equivalent of about 40 drops from 6 ft.

In the *Cochrane Abrasion Test* 25 lb of coke is rotated in a small drum to 1000 revolutions. The percentage + ⅛ in. is quoted as an abrasion index and should be about 80. This test involves even more abuse than the other tests.

If coke is subjected to an increasing number of equal "blows" its statistically determined average size $\bar{x}$ is found to decrease linearly as the logarithm of the number of blows increases (Fig. 2). This means that any strength test like those described is very sensitive to previous history and a sample which has already been roughly handled is likely to appear strong in the test. This is because much of the breakdown is by the propagation of preformed cracks. Once these are used up new cracks are not readily formed.

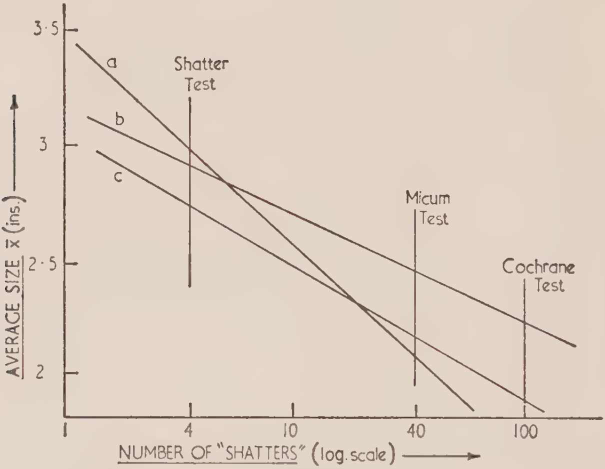

Fig. 2. The effects of the Shatter test, the Micum test and the Cochrane test on the statistically average size $\bar{x}$ of (a) a large weak coke, (b) a large strong coke, and (c) a smaller strong coke. It can be demonstrated that the 100 turns of the drum in the Micum test does damage equivalent to 40 Shatters and that 1000 turns in the Cochrane drum is equivalent to 100 Shatters. Note how (a) and (b) are assessed differently by the Shatter and Micum tests.

The initial breakdown, as in the Shatter testing of "fresh" coke, is apparently very severe, but that of well-handled coke is less so. The difference in the breakdown in the Micum and Cochrane tests between fresh and partly broken coke is not so great as in the Shatter test. If the initial size is large but the slope in Fig. 2 steep, the Shatter test will indicate good coke, but if the initial size is small and the slope is shallow (a much better coke) the Shatter test might show the coke to be relatively poor. In these cases Micum tests might give quite the opposite impression if the lines crossed between the Shatter and Micum ordinates, as do (a) and (b) in Fig. 2.

The tests are obviously not satisfactory except as control tests on fairly regular production. An alternative scheme of testing has been suggested whereby the actual size at the blast furnace is determined and possibly a further breakdown test applied here to simulate damage within the furnace.

The determination of an average size parameter as used in Fig. 2 is not easy because coke sizes are distributed in a bimodal distribution. The parameter $\bar{x}$ already mentioned referred to the modal size of the large material, and ignored the 5 per cent or so of "fines" which become important only after much damage has been inflicted.

Real density is determined by water displacement in a density bottle and indicates the thoroughness of coking—the degree of graphitization. The value should approach, or slightly exceed, 2·0. This quantity is not readily determined with accuracy. The sample must be finely pulverized to ensure access to the whole pore volume. The coke must be thoroughly degassed by evacuation before the water is admitted to fill it up. Other displacement fluids give slightly different results as they are adsorbed to different degrees on the extensive inner surface of the coke. Helium displacement, a special technique, gives the highest and probably truest value, as helium is not adsorbed on the coke surface but can readily effuse into the innermost pore space.

Apparent density is the mass per unit volume of coke including pore space. This must be determined on lumps and good reproducibility is impossible to attain as lumps can be very different one from another. The usual method involves soaking a known large mass of coke in paraffin oil and then determining its volume by water displacement, assuming that the oil stays in the coke and properly defines its limits. This method leaves much to be desired in absolute accuracy. The best method is to cut prisms of coke, weigh each, seal off the pores with wax and determine volume by displacement. Each determination is then accurate but adequate replication is needed to yield an accurate mean. The apparent density of coke is about 1·0.

Porosity is calculated from real and apparent densities and its accuracy is subject to the errors in each of these. Its value lies in the range 45–55 per cent and is often close to 50 per cent. It was once considered that porosity might affect reactivity but the total range is so small that the effect would have to be through pore-surface area, which depends on pore-size distribution. These areas do vary between cokes but the largest specific surface areas encountered are probably not much greater than twice those of the smallest. Porosity is now believed to have only a minor effect on reactivity.

Bulk density is the mass per unit volume including voidage between lumps, and is usually determined by weighing a level wagon-load. It is of interest as a factor for converting volumes to weights when charging is on a volume basis. Corrected to a standard apparent density it is also a sensitive index of strength—or rather of degree of breakdown—and one authority has claimed that coke bulk density correlates better with blast-furnace performance than any other property.

The quality of coke is very much tied to the nature of the coal from which it was made and the results of these tests are barely adequate to describe the differences between cokes made from South Wales, Durham, Yorkshire and Scottish coals. Under test or under the microscope they often seem rather similar while the practised eye or ear can easily tell that they are quite different.

6. Gaseous Fuels

Gaseous fuels are popular both industrially and domestically for their cleanliness and flexibility. Most users buy their gas from their area Gas Boards who are responsible for all the manufacture, storage and distribution problems which become most severe in the winter months when demand reaches its peak. These seasonal difficulties are gradually being alleviated by the establishment of area gas grids and the replacement of local piping. Massive underground storage in suitable porous strata is also planned to help to meet the peak demands out of savings rather than out of current production. The largest consumers, such as the steel industry, make their own gas, producing to their own requirements a cheaper if often a cruder fuel.

The use of gaseous fuel has the advantages that there is no ash to dispose of (unless of course the gas is made by the user) and no smoke is produced. It can be tapped in large or small amounts and if bought from the Gas Board can be expected to be of a regular quality and constant calorific value. It can be burned by a variety of techniques to short hot flames or to long lazy flames to meet a wide range of requirements.

Classification

Gaseous fuels are available from a variety of sources:

1. Natural—from oil and coal measures.
2. From carbonization plants.
3. From "gas producers", from coal or coke.
4. By cracking of oil.

5. From blast furnaces.
6. By bacterial decomposition of sewage (for use in sewage plant).

Production

Natural gas has been exploited most fully in the U.S.A. where it is piped from the oilfields for distribution over a large part of the country and its export, liquefied, and in tankers, has been demonstrated to be possible. The supply of natural gas from the Sahara to Europe seems a likely development in the near future but large quantities in the Middle East are lost because there are no users sufficiently near. Only small amounts of natural (oil) gas have been tapped in Britain.

The methane of coal measures can also be tapped off prior to mining. In Germany this practice is well established but only about 15 per cent of the gas is actually recovered. Methane equivalent to about 18,000 tons of coal a year is being drawn from seams in Staffordshire and similar smaller schemes are in operation in Scotland and elsewhere. They are being applied first where the coals are gassy partly as an aid to safer working. The gas taken off is usually fed into the area gas grid, after colliery requirements have been met.

Producer gas is manufactured by total gasification of coal or coke in a gas "producer" or "generator". This is a refractory-lined cylindrical reaction vessel fed with solid fuel at the top against a stream of ascending gas derived from air or steam or both, injected or drawn in through the bottom. The reactions take place at about 1000°C or over and the gas produced is drawn off at 700–800°C. The important reactions which occur are:

(1) The "producer gas reaction". $2C + O_2 = 2CO + 53{,}200$ cal.

(2) The "water gas reaction". $C + H_2O = CO + H_2 - 32{,}300$ cal.

Actually (1) occurs in two stages:

$$\text{(1a)}\quad C + O_2 = CO_2 + 94{,}200\ \text{cal.}$$
$$\text{(1b)}\quad CO_2 + C = 2CO - 40{,}800\ \text{cal.}$$

and the bed must be deep enough that the second is almost completely accomplished. If the fuel bed is not hot enough, i.e. below about 800°C, (1b) will go too slowly and a part of the carbon will not be available as a gaseous fuel. The producer gas reaction yields a theoretical product 67 per cent N_2 and 33 per cent CO accompanied in practice by a little CO_2 and hydrogen, methane and tarry matter in quantities depending on the nature of the coal or coke gasified.

Reaction (1) is strongly exothermic so that the producer runs very hot. The gases come off at up to 750°C and are often used immediately as in open-hearth steel furnaces to utilize the sensible heat. The fuel bed also becomes very hot and clinkering of ash is likely to cause inconvenience in its withdrawal at the bottom of the producer.

The excess of heat over that needed to maintain a reasonable temperature may be absorbed by water jacketing and running the unit as a waste heat boiler. More usually steam is injected with the air so that the endothermic water gas reaction (2) can absorb the excess heat. The calorific value of the gaseous product is raised as nitrogen is replaced by CO and H_2 in equal proportions.

The optimum proportion of steam to air is primarily decided by the thermal balance but side effects arise if the proportion of steam injected is too high. Particularly, the temperature of the bed falls and the CO_2 content of the gas is increased by the reaction:

$$CO + H_2O = CO_2 + H_2$$

as the partial pressure of H_2O rises. The H_2O content of the gas produced becomes unduly high and its calorific value falls. The amount of steam used is usually about 0·4 lb per lb of fuel unless severe clinkering makes cooler operation essential.

Gas producers may be fed with almost any carbonaceous fuel but the important choice is between coke and anthracite on the one hand, which gives permeable fuel beds and clean gas, and weakly caking bituminous coal on the other, which does not swell and choke the fuel bed, but yields a tarry gas burning with a good luminous flame. If impermeable beds are formed air should be supplied under pressure and the hearth rabbled to maintain gas flow. The producer coal should be well sized for good permeability coupled with large reacting surface area.

Producer gas with its high nitrogen content (see Table 5) has a very low calorific value and, when burned with air, provides low flame temperatures unless considerable preheating of both gas and air is employed. Producer gas made with oxygen enriched air and steam would have a much higher calorific value. The generator would run at a higher temperature but some of the heat could be put toward steam-raising. Producers using oxygen and steam are operated so that the coal ash is melted or slagged for easy removal from the generator. The gas obtained from these producers is usually rather high in CO_2 and its calorific value is only about 2000 kcal/m^3.

Water gas is sometimes required undiluted with nitrogen, particular applications being in reheating furnaces for forging and forge welding of steel. Water gas generators operate by a two-stage cycle. Air is blown through the fuel bed to heat it up beyond 1000°C, the products of this stage being passed to the chimney. The second stage is to blow steam through the incandescent coke until the temperature falls to about 900°C, the gas being fed to a gas holder which is necessary to accommodate an intermittent supply to a constant demand. When the temperature falls to 900°C the steam is cut off and air again blown.

The product is known as "blue" water gas. Its uses are rather restricted but it can be more easily used to higher temperatures than producer gas and it is also used as a source of hydrogen for the chemical industries.

Carburetted water gas is a more important fuel; it is enriched with cracked oil vapour. In this case, the producer gas made during the air blow is used to heat up a carburettor and cracking chamber. This latter is a hot box of chequer brickwork, held at about 800°C. During steaming, oil is sprayed into the water gas stream as it enters the cracking chamber and about three-quarters of it is decomposed to variable mixtures of methane, ethane, unsaturated hydro-carbons and hydrogen. The remainder forms tar which would usually be recovered, and char which helps to heat the chequers in the heating stage following. The gas oil used is a light fraction boiling at about 200°C. The ratio of coke to oil is about 3 : 1 by weight. The gas produced has an enhanced calorific value and can be used as a component of town's gas. This type of generator is flexible in operation, and by replacing coke with oil reduces the demand for coking coal for gas production.

Oil gas is made by a similar process but from heavy oil which may require to be decomposed catalytically in the carburettor. It may or may not be mixed with water vapour. Its calorific value is very high. It has been used as a town's gas but has been displaced in the U.S.A. by natural gas, and for other purposes by bottled gas.

Blast-furnace gas is a low-grade producer gas available in vast quantities at iron-works. Thoroughly cleaned of dust it is used extensively in integrated steel plant for Cowper stoves, steam-raising for power, reheating furnaces and even in gas engines for driving blowers or electricity generators. Modern blast-furnace practice tends to reduce still further the calorific value of this fuel but the total potential heat is still large and the gas will continue to be utilized even if it has to be enriched slightly with coke-oven gas. The most recent developments in blast-furnace practice—fuel injection, oxygen enrichment and steam injection—may result in an increase in the calorific value of the top gases mainly due to a fall in nitrogen and a rise in hydrogen content.

Retort gas is the gaseous product of carbonization of weakly coking gas coals. It is rich in hydrogen and methane and has a high calorific value and as the traditional basis of town's gas is widely used both in homes and by industry. "Steamed" retort gas has a higher carbon monoxide content and a slightly lower calorific value. The toxicity of the carbon monoxide is the greatest disadvantage of this gas especially in view of its very wide distribution.

Coke-oven gas is similar in composition to retort gas and is used in the steel industry for many purposes. It cannot be preheated because the methane would crack in the regenerator chambers and deposit soot. It burns with a clear, non-luminous flame with poor radiation properties and must be used with some oil to produce luminosity. Open-hearth furnaces are often fired with a mixture of coke-oven gas and oil or coal-tar fuel or pitch.

Refinery gases are the light hydro-carbons fractionated from petroleum oil. These are the C_2, C_3 and C_4 hydro-carbons, but some C_3H_8 (propane) and C_4H_{10} (butane) would normally be separated for sale as "bottled" gas. The residue could be mixed in with town's gas either unchanged if the addition was to be small, or as *reformed gas* if a large addition was to be made. Reforming is a partial combustion with the aid of alumina as a catalyst at about 850°C—

$$2CH_4 + O_2 = 2CO + 4H_2$$

Butane and *propane* from petroleum are liquefied and distributed in cylinders for use in homes, caravans and to an increasing extent industrially, e.g. for welding. Their calorific values are very high and very hot flames can be produced using them.

Non-explosive butane–air mixtures can be safely piped for use in compact communities if suitable burners are used

Town's gas supply is traditionally based on gas retorts but usually a part of the coke produced is gasified to water gas or carburetted water gas for mixing with the retort gas. Any of the other gases mentioned might be added in also, provided the declared calorific value is maintained and the gas supplied can be used safely in the standard burners. Town's gas is distributed in accordance with a number of legal safeguards and regulations. These cover toxicity (H_2S and HCN but not CO) and calorific value particularly. It is available for both domestic and industrial use but many industrial users find it too dear and prefer to make their own gas, probably less pure but equally satisfactory. Some fortunate industrial areas have a gas grid through which all large gas users and makers are linked to their mutual benefit. Distribution is no longer under control of the "town", of course, but is the responsibility of the Area Gas Board.

Complete gasification of coal in one stage to a high calorific value gas suitable for use as a town's gas has long been the aim of several processes. One process which has had some success even with low-grade coals is the *Lurgi* process which may have a place in future developments. A full-scale "experimental" plant is now operating in Fife and supplying the Scottish gas grid.

Fine coal is gasified in a producer operating at 1000°C and 20 atmospheres pressure by reaction with an oxygen steam mixture. The product is like steamed retort gas but with a higher CO_2 (30 per cent) content which must be scrubbed out. It contains about 15–20 per cent of methane and other hydro-carbons which are probably formed by hydrogenation of the tars under pressure. At higher temperatures the CO_2 might be reduced to smaller proportions but clinker formation limits the temperature that can be used. The great benefit of such a system is that low-grade and non-caking coals can be transformed into high-grade gaseous fuel.

Among minor sources of gaseous fuel the most interesting is underground gasification which would reduce the labour of mining if developed to complete success. Air, or air and steam, are pumped into thin unworkable seams and made to react as in producers. The gas drawn off from an adjacent part of the seam is a lean producer gas. A higher calorific value could be obtained by using oxygen-enriched air with steam. Various schemes to develop these ideas have shown some promise but none has yet led to large-scale operation.

Properties and Uses

Typical analyses of gaseous fuels are presented in Table 5 with their calorific values. They fall into three distinct groups. The straight hydro-carbons derived from petroleum have very high calorific values ranging from 9000 kcal/m^3 for gas which is essentially methane, up to nearly four times that figure where the major constituent is butane. The difference is, of course, mainly due to density, the C_4 hydro-carbon being about four times as dense as methane when in the gaseous state. Expressed as calories per gramme these figures all become similar to those for liquid fuels, gasoline and kerosene in Table 6.

Those manufactured gases which are prepared so as to be low in nitrogen have calorific values about 3000–4000 kcal/m^3 and are the ones which are normally referred to as "rich" to distinguish them from the lean fuels with 50–60 per cent nitrogen and calorific values around 1000 kcal/m^3.

Obviously members of these three groups can be expected to behave differently and cannot be interchanged or intermixed without some adjustments being made to equipment or practice. Bottled gas and town's gas for example require quite different burners at the domestic level. Producer gas and coke-oven gas also need very differently shaped "ports" in steelmaking furnaces. Producer gas should be preheated for most purposes while those gases rich in methane and other hydro-carbons cannot be preheated without cracking. In fact, mixed firing is frequently practised and different types of gas are blended for public distribution, but not without appropriate precautions being taken.

Gas continues to compete successfully with oil and electricity in many industries. It is clean and can be almost completely desulphurized if necessary. It need not require on-site storage facilities, warming equipment or injection steam like oil. Gases can be burned with extreme intensity and can give very high heating rates particularly if convective transfer of heat to the charge can be tolerated. The use of methane or propane with oxygen in "fuel lances" is being developed. These new techniques

TABLE 5

Typical Analyses of Fuel Gases in Per cent by Volume and their Approximate Calorific Values

	ANALYSIS								NET CALORIFIC VALUES	
	H_2	CO	"CH_4"*	"CnHm"*	CO_2	O_2	N_2	Others	kcal/m^3	B.t.u. /ft^3
Natural gas	—	—	90	C_2 C_3 C_4 3 1·5 0·5	1	—	3	—	9000	1000
Refinery gas	8	—	10	C_2 C_3 C_4 10 45 20	—	—	—	H_2S:7	18,000	2000
Domestic bottled gas	—	—	—	C_2 C_3 C_4 3 22 75	—	—	—	—	30,000	3400
Coke oven gas	54	7·5	28	2·5	2·5	0·5	6	—	4000	450
Retort gas (coal)	52	9	28	3	2·5	0·5	5	—	4250	475
Retort gas (steamed)	50	18	20	2	4	0·5	5·5	—	3800	425
Blue water gas	49	41	1	—	5	0·5	5	—	2500	275
Carburetted water gas	37	30	14	7	6	—	5	—	4000	450
Oil gas (steamed)	48	19	14	6	8	0·5	4·5	—	4450	500
Producer gas (coal)	12	29	2·5	0·4	4	—	52	—	1350	150
Producer gas (coke)	11	29	0·5	—	5	—	54·5	—	1100	125
Producer gas (air only)	1	33	—	—	1	—	65	—	900	100
Blast furnace gas	1	27	—	—	11	—	61	—	800	90
Lurgi gas (scrubbed)	50	19	22	1	7	—	1	—	4000	450

* Methane may include a little of other paraffins. The composition of the unsaturated hydro-carbons varies from one fuel to another.

produce something like electric arc conditions from the combustion of a gas.

The products of combustion of gases are a vehicle for the transfer of waste heat to recuperators, and here is a positive advantage over electricity. Gases are also used, only partly burned, as reducing atmospheres in metallurgical furnaces to prevent oxidation or decarburization of stock and even as reducing agents in extraction processes.

The uses of gas for heating purposes are without number, and range from domestic heating up to steelmaking. It is also used as the source of power in gas engines which may produce electricity or drive locomotives. It can take part in metallurgical reactions or may be used as the starting point—as crude hydrogen, carbon monoxide or methane—in many heavy chemical processes. The oil industry has certainly invaded many of the preserves of the gas industry in recent years but it would appear that as the economy expands both kinds of fuel will continue to be required together for a long time.

7. Liquid Fuels

Classification

Liquid fuels are mainly oils, tars and pitches and are derived from the following sources:

1. Petroleum
2. Oil Shales
3. Coal, by carbonization
4. Coal, by hydrogenation

At present petroleum provides the majority of our liquid fuel requirements. The reserves of oil shales are immense, however, and these will probably increase in importance in the future. The liquid and tarry products of carbonization are used by industry near coalfields and carbonizing centres and, as a result, the steel industry employs these in fairly large quantities. Hydrogenation of coal has been exploited mainly by the Germans using lignites. It competes economically with oil only with great difficulty but the process has had strategic significance.

Production

Petroleum is available in many parts of the world and new sources of supply still continue to be found. The crude oils from various parts of the world have a lot in common and their ultimate analyses do not differ greatly from one oilfield to another, with carbon at about 84 per cent ± 3, hydrogen 13 per cent ± 1, sulphur up to about 3 per cent, and perhaps 0·5 per cent each of nitrogen and oxygen. All these crude oils consist of mixtures of hydro-carbons—paraffin, olefines, naphthalenes and aromatics ranging from the simplest gaseous members of the homologous series to complex waxes and bitumens—all interdissolved.

The crude petroleums do differ, however, in that some are predominantly paraffins and distil to leave a residue of paraffin wax, while others are mainly aromatic and yield an asphaltic or bituminous residue on distillation. Others have a lot of naphthalenes present, and every classification is based on the proportions of these three components. These differences are important to the refiner who has to sort out the components by distillation into useful groups and if necessary modify these chemically, so that the yields of the various fractions roughly match the demands of industry for them. It is not, however, suggested that all petroleum is divided neatly into a small number of sharply defined fractions. There is obviously much overlapping and room in which to manoeuvre to satisfy the market. The market is not, however, as regular as the composition of petroleum and other operations, apart from fractional distillation, are applied either to break down heavy hydro-carbons into lighter ones (cracking) or to build the lighter ones into others with larger molecules (polymerization). These operations can also modify the proportions of different types of molecules, long chain, short chain, branched and aromatic ring types for example, so modifying the properties of the fuel in any boiling range bracket. A high-octane number (anti-knock index) in petrol is obtained if the proportion of branched molecules is high, for example.

Refining is the fractionation of the petroleum into its components and the first stage is a simple fractional distillation as follows:

1. Natural gas—Boiling range below 30°C. This is usually removed under reduced pressure at the oilfield, initially to permit safe handling of the crude oil.

2. Gasoline—Boiling range 30–200°C. This is "petrol" and may be further divided into aviation spirit (30–150°C), motor spirit (40–180°C), and vaporizing oil (110–200°C) for tractors, etc.

3. Solvent spirit—Boiling range 120–250°C. This is white spirit or turpentine substitute and is used as a solvent, a cleansing agent and in paint manufacture.

4. Kerosene—Boiling range 140–290°C. This fraction includes domestic paraffin oil (140–250°C) and heavier slow-burning fractions used as illuminants in railways (signal oil) and in lighthouses.

5. Gas oil—Boiling range from 180°C and leaving a residue of carbon at 350°C. This is used as a carburetting oil in the gas industry and also in diesel engines.

6. Fuel oils—Boiling above 200°C. Beyond this point vacuum distillation is necessary to avoid cracking of these heavy oils with the formation of lighter oil and carbon residue:

7. Light fuel oil—Boiling above 200°C.

8. Heavy fuel oil—Boiling above 250°C.

These are fractions of interest to furnace operators—for use in ships, land boilers, metallurgical furnaces, etc.

9. The residue from these stages is becoming very thick and yields on further treatment, if paraffinic, wax (paraffin wax), mineral jelly ("Vaseline"), and lubricating oils and greases or, if asphaltic, bitumens and lubricants.

Early *thermal cracking* techniques were developed about a century ago to use up superfluous heavy oils in the production of light paraffins for illuminants. Very brief heating at 400–500°C caused some charring but had the desired effect. Higher temperatures produced more gaseous products or polymerization to aromatics if above 700°C.

Today the accent is on producing gasoline rather than kerosene, but future developments in engine design may well shift the demand on to diesel fuel (gas oil) for internal combustion and jet engines.

The modern techniques are by *catalytic cracking* which gives greater control over the reactions occurring. The product can be controlled through temperature, pressure, catalyst and time of contact. Catalysts used in this stage were originally specially prepared bentonite clays but now tiny granules of synthetic alumino-silicates are employed and fluidized bed techniques are used to put the process on a continuous production basis. The cracking temperature is about 500°C. Poisoned catalyst is continually revived by burning off the char as it is passed round a regeneration cycle.

Further treatments may be applied to improve various fractions. *Reforming* is either a thermal or a catalytic treatment to improve straight-run gasoline or convert naphtha to gasoline. Catalysts used include platinum and oxides of aluminium, chromium and molybdenum. The aim is improved petrol with good anti-knock properties for high compression ratio engines, and this is achieved by increasing the proportion of branched hydro-carbons and aromatics.

Catalytic polymerization usually aims at combining olefine molecules in twos and threes to convert gaseous olefines to liquids for the gasoline fraction. Treatment with sulphuric or phosphoric acid is employed. *Alkylation* is a specialized combination of olefine and hydro-carbon molecules to give complex branched molecules characteristically anti-knock. Various acids act as catalysts for these reactions.

Any fraction may be purified by washing with reagents. Sulphuric acid removes unsaturated hydro-carbons and some sulphur compounds. Sodium hydroxide and lead dioxide react with sulphur compounds and remove sulphuric acid. Such processes are expensive and the cost of each operation must be justified by improved performance of the product. They are not likely to be applied widely to the heavy fuel oils though for metallurgical use a treatment to reduce sulphur would be worthy of consideration and would have an easily calculated economic value.

Oil shales provide only a tiny fraction of our oil requirements today, although the oil industry in Britain originated in the shale mines in the Lothians. Until 1962 this remained the only major shale oil producing area in the world with an annual output of 100,000 tons but production has now ceased. The oil produced was paraffinic and was treated in exactly the same way as petroleum after the initial distillation. There are vast reserves of oil in shales particularly in the U.S.A. and U.S.S.R.—greater than the known reserves of petroleum. It seems likely that these will ultimately be used.

Coal tar liquor is important to the steel industry which is usually situated near coalfields and carbonizing plants.

The tar may be distilled to the following fractions:

1. Light oils—b.p. up to 170°C yielding benzene and naphtha.
2. Carbolic oils—170–230°C, yielding phenols, naphthalene, etc.
3. Creosote oil—230–270°C, yielding motor-spirit, tars, acids.
4. Anthracene oil—270–320°C, yielding anthracene, etc.
5. Residual pitch which may be further distilled to yield hard pitch or pulverizable coal tar fuel.

While valuable chemicals are available in these products, the demand for them is limited and a large part of the tar is prepared into a series of standard coal-tar fuels designated C.T.F. 50, 100, 200, 250, 300 and 400. The number indicates the temperature in °F at which the blend is fluid enough for atomization (i.e. a maximum viscosity of 0·25 stoke).

C.T.F. 50 and 100 are blends of fractions (2), (3) and (4) above. C.T.F. 300 is a blend of (5) and (4) with varying amounts of (3) achieved by stopping distillation at an appropriate stage, while C.T.F. 200 and 250 are made by "oiling back" blend 300 with further additions of (3). C.T.F. 200 is the most popular blend. These fuels have high calorific value, low ash and sulphur content and give good luminous flames. They may not be mixed in tanks or pipelines with petroleum fuels, as tars are precipitated.

The final residue of hard pitch may be used as a pulverized fuel after comminution in an air-swept swinging hammer mill. It is obviously economically desirable that all these organic residues should be burned if possible.

The hydrogenation of coal to produce fuel oil is not at present important in this country and has been employed elsewhere only for making motor and aviation spirit and other light oils rather than those of metallurgical interest. The process involves autoclaving coal with hydrogen at about 500°C and 200 atmospheres pressure, and distilling the product. It can be applied also to other carbonaceous matter—e.g. oil, pitch, etc.

Special Tests on Liquid Fuels

Flash point is the minimum temperature at which the oil will catch fire if exposed to a naked flame. Minimum flash points are stipulated by law for various grades of oil (> 80°C for fuel oil), and values are determined in a standard apparatus (e.g. Pensky–Martin) used in a standard manner. The test is primarily carried out as a safety precaution, but would also indicate deviations from specification.

Viscosity is also determined in standard equipment as a check on specification as regular behaviour in pipelines and burners is desirable. Viscosity varies logarithmically with temperature and would best be determined over a range of temperature. The Redwood Viscometers (I and II) comprise an oil cup in a water jacket which can be temperature controlled. When conditions are stabilized the oil is allowed to flow through a standard orifice in the base of the cup and the viscosity is expressed as the number of seconds for the first 50 ml to flow. When the efflux time in I exceeds 2000 sec viscometer II is used, in which the orifice is wider and the time is reduced by a factor of 10. Conversion of Redwood (I) seconds to centistokes is by a factor of about 0·25 which is not, however, constant over the range. Viscosities of fuel oils lie in the range 250–7000 Redwood (I) seconds at 100°F (37·8°C). More viscous fractions are cracked to lighter components. Oil can be pumped at a viscosity of about 3000 sec. but must be warmed to 100 sec. before it can be atomized. Steam for atomizing provides some of the necessary heat.

Other determinations of special interest include density and its variations with temperature to provide an accurate conversion factor for volume to mass, especially if liquid fuels are metered and bought by volume. Specific heat data are also useful for assessing heat requirements when warming oil to atomizing temperature.

Properties and Uses

The properties of a selection of liquid fuels are arranged for comparison in Table 6. It will be observed that the sulphur is concentrated in the heavier fractions of the petroleum oils. For many purposes this is unimportant. It is, of course, an advantage to the user of the light fractions. In steelmaking, however, the high sulphur content of fuel oil is probably its most objectionable feature and sets oil at a disadvantage compared with coal-tar fuels. Ash also concentrates in the heavy fractions but not so far as to be of significance in furnace work.

The calorific values of all fractions are similar and oils have rather a higher calorific value than coal-tar fuel, and a considerably higher value than coal, especially if translated to a (bulk) volume basis. These differences are due to the higher oxygen and ash contents of tar and coal.

It will be apparent that the viscosities of heavy oils vary over a tremendous range and it will be obvious that for convenience in furnace operation a supply of fuel of an almost constant viscosity is highly desirable. Some adjustment can be made through temperature but this should not be necessary except under unusual circumstances. Fuel oil is most commonly specified by viscosity at one or more temperatures. There are British Standards Specifications for fuel oils which can be ordered by naming the appropriate standard grade. Alternatively, closer specifications can be demanded and can usually be met by blending. In other countries similar standard grades are specified also. Major differences might arise in the oils offered by different companies if these originated in different oilfields. Thus, one oil might be essentially paraffinic and another asphaltic, and these might be expected to behave slightly differently in the furnace especially in the last stages of

Table 6

Properties of Some Liquid Fuels

	Motor gasoline	Motor benzole	Kerosene	Diesel (gas) oil	Light fuel oil	Heavy fuel oil	C.T.F. 200	Bituminous coal (for comparison)
Carbon %	85·5	91·7	86·3	86·3	86·2	86·2	90·0	80·0
Hydrogen %	14·4	8·0	13·6	12·7	12·3	11·8	6·0	5·5
Sulphur %	0·1	0·3	0·1	1·0	1·5	2·0	0·4	1
Nitrogen %	—	—	—	—	—	—	1·2	1·5
Oxygen %	—	—	—	—	—	—	2·5	7
								5 (Ash)
Specific gravity (15°C)	0·73	0·88	0·79	0·87	0·89	0·95	1·1	1·25
Kinematic viscosity:								
20°C cS	0·75	0·72	1·6	5·0	50	1200	1500	—
Redwood I sec	—	—	—	—	200	5000	6000	—
100°C cS	—	—	0·6	1·2	3·5	20	18	—
Redwood I sec	—	—	—	—	30	90	80	—
Boiling range °C	40/185	80/170	140/280	180/—	200/—	250/—	200/—	—
Residue at 350°C %	—	—	—	15	50	60	60	—
Flash point °C	– 40	– 40	39	75	80	110	65	—
Calorific value (net) cal/g	10,450	9600	10,400	10,300	10,100	9900	9000	7750

combustion. They might also differ somewhat in appearance, in ash content, and in the nature of the ash. Differences of this kind are of greater importance when the oil is being used as fuel for engines.

The uses of oils are as varied as those of gas and include domestic heating and lighting, steelmaking, all kinds of engines, the generation of electricity, and the production of gas. Oil is also used as a raw material in the chemical industries. It can be almost as clean as gas in use but spillage and leaks of thick oil and tar are unpleasant features of many plants. The need for steam for warming the storage tanks and pipelines and for injection through the burners involves the use of space and money and the delivery of oil in quite small and very frequent batches by road tanker necessitates some careful organization and numerous checks on quality.

Oil can be burned to very intense hot flames, especially if used with oxygen-enriched air. In this respect only the very rich gases can be expected to do as well. On the other hand, oil flames are luminous and radiate heat very effectively while rich gases burn to clear non-luminous flames and tar or oil must be added to provide luminosity. Coal-tar fuels give flames which have particularly good luminosity and heat transfer rates.

The use of oil has increased in recent years and it has apparently displaced coal and gas from some of their traditional preserves. In fact the supply of oil has expanded more rapidly than that of coal to meet the rapidly increasing demand for fuel of any kind, and it may be worth observing that while oil is replacing gas in, say, steel plant, it has itself virtually disappeared as an illuminant, having been replaced first by gas and then by electricity. The advantages of oil in steel plant were primarily that it was available at a critical period when coal was scarce and secondly that oil benefited from the post-war developments in steelworks fuel technology and now stands in a very strong position compared with gas. Higher production rates are being obtained (partly due to other causes such as the use of tonnage oxygen) and much of the industry is geared to its use. The advantages of oil over gas or coal in other fields is not so substantial, however, and at the level of domestic central heating, for example, the significant differences between gas, oil and coke-fired appliances are likely to be commercial rather than technological or economic.

8. Electrical Energy

Electrical energy is not a fuel but is a substitute for fuel and replaces it (or displaces it) in many industrial applications.

Sources of Power

Electricity can be generated from several sources of energy.

1. By conversion of chemical energy in coal, oil, peat or other conventional fuels into heat by burning, into mechanical energy by steam-raising, and then to electrical energy by using a turbine and dynamo.

2. By conversion of the potential energy in water in elevated reservoirs to kinetic energy in raceways and then to mechanical and electrical energy using turbines and dynamos.

3. By similar conversion of the kinetic energy in wind.

4. By conversion of nuclear energy via heat and steam.

5. By the use of electrolytic cells and fuel cells in which chemical energy can be converted directly to electrical energy.

Method (1) predominates in Britain and in most of the highly industrialized countries where coal is plentiful. The most modern boiler plant uses low-grade pulverized coal to produce steam at up to 850°C and 2000 lb/in.^{2} pressure. Steaming rates are very high at up to nearly 4 million lb/hr equivalent to about 200 tons of coal per hour, and the efficiency of energy conversion can be as high as 88 per cent at this stage. The modern furnaces do not use banks of water tubes athwart the combustion gas stream and relying on convection for heat transfer. These have been replaced by a jacket of water tubes placed round the walls of the combustion chamber and heated mainly by radiation from the luminous flame of the pulverized coal burned to a very high temperature with preheated air. The steam is expanded through the stages of a large turbine mounted on the same axis as the generator, the low-pressure side being almost a vacuum imposed by the condenser. The overall efficiency rises to about 38 per cent in best practice but the average is much lower and must remain so until the oldest plants working at under 20 per cent efficiency are replaced. The most efficient new plants, called base load plants, are designed to run at over 80 per cent capacity for 24 hours per day, peak loading of the grid being built up using the older units.

In Britain, water power has been developed mainly in Scotland but the total available energy is not high and further exploitation is likely to be at rapidly increasing cost both in cash and in "amenity". Other more mountainous countries develop a much higher proportion of their power requirements from water power but these often find shortages developing either due to drought or to frost. Though tidal water power has long been discussed it has not yet been harnessed but one move is now afoot in France and another in Mauritius to do so. Meanwhile it is the large continental rivers which are being tapped—a matter of considerable importance for underdeveloped Africa and Asia. At present much of the hydro-electric power developed in Britain is "switched on" at peak loading periods, the main load being carried by conventional coal-steam stations. At three stations hydro-electric power is produced especially for the electrolytic extraction of aluminium. Wind power has been generated for very local use in Orkney, and on a domestic scale elsewhere, but extensive development is unlikely to take place.

The generation of electricity from nuclear energy is still in its infancy. The technology can be expected to make further big advances in the next few decades but already programmes of construction of nuclear power stations are in hand in Britain and extensions to the programme planned well ahead. All reactors use uranium as the primary fuel. The uranium may be natural, mainly ^{238}U, or it may be enriched with respect to the ^{235}U isotope of which there is only 0·7 per cent in the element as mined. Neutrons, which arise spontaneously in radioactive materials under the internal bombardment of their own radiations, can cause the disintegration of atoms of ^{235}U into two smaller atoms, with the release of one or more further neutrons and other radiations, the energies of which are largely convertible to heat. The mass of the parts formed in any disintegration is less than that of the original uranium atom by a small amount δm which is related to the change in the internal bonding energies δE by Einstein's equation $\delta E = \delta m\ c^2$, where c is the velocity of light. The neutrons released may escape the system if it is small, or they may be absorbed by ^{238}U atoms to form a new isotope ^{239}U, or they may collide with ^{235}U atoms to cause further disintegration and more new neutrons. If, on average, one neutron from each disintegration brings about one other disintegration, a chain reaction has been established and the process is self-sustaining. The energy released can be withdrawn as heat and put to useful work. Actual operation of an atomic "pile" depends on conditions being arranged so that a much higher proportion of neutrons brings about disintegrations than will ever occur in a large piece of natural uranium because the ^{238}U absorbs too many of them. The effective proportion depends on the geometric design, the neutron energies and the kinds of atoms present. It can be increased by using a more spherical form so reducing the escapes per unit volume, but greater increases are effected by increasing the proportion of ^{235}U (enriched fuel) or by slowing up the neutrons by passing their radiations through materials called "moderators", light elements carbon, beryllium or deuterium, which slow up the neutrons to so-called "thermal" energies. They are then more likely to react with ^{235}U and less likely to be absorbed by ^{238}U. The core of a so-called "slow" reactor is a lattice made up of a large mass of moderator permeated by rods of fuel which may or may not be slightly enriched. The fuel itself must be kept free of impurities which would absorb neutrons without producing heat. Disintegrations of course produce such impurities and the fuel must be purified of them periodically—a difficult and expensive chemical operation, especially considering the highly radioactive nature of all the materials involved. When the proportion of ^{235}U is high—over about 25 per cent—a "fast" reactor may be operated with no moderator beyond the uranium itself. This type of plant would be quite compact and it could produce heat just as fast as it could be withdrawn from the pile. If the excess of neutrons or those escaping from the core can be captured by ^{238}U, some plutonium can be produced which can be extracted chemically and used as the fuel in another fast reactor of suitable design, since plutonium is similar to ^{235}U in that it is readily disintegrated by neutron bombardment. The reactor producing the plutonium is called a "breeder" reactor.

Control of the output of a reactor is effected by means of control rods. In slow reactors these are made of steel and act by absorbing a high proportion of the neutrons they encounter. In fast reactors the rods are fuel elements and the activity is reduced or stopped by reducing the mass of the fuel below a critical value necessary for maintenance of the chain reaction. The heat developed is removed from the pile by the circulation of a suitable fluid through a heat exchanger designed into the pile and used to make steam in another exchanger external to the pile. Carbon dioxide and liquid sodium have been used as heat transfer media, the latter, having the higher heat capacity per unit volume, being used in the more compact fast reactor.

There are still many metallurgical problems only partly solved pertinent to the operation of the reactors and research is being carried out into the best forms of both the moderators and the fuel elements and to find whether pure metals, alloys or refractory compounds are likely to be the most suitable for operation at higher temperatures. At present the physical properties of the materials used limit the operating temperature to about 500°C, which puts the generation of power from atomic energy at a severe thermodynamic disadvantage compared with conventional methods.

Fuel cells are in an early stage of development. They might soon be available for small-scale generation of electricity but are not likely to replace conventional power stations in the near future. Direct conversion of nuclear energy to electrical energy is also a pipe dream which may one day come true. Such direct conversions which do not involve heat as an intermediate stage can, theoretically, be carried out with, almost, 100 per cent efficiency. The Carnot cycle limitation does not apply.

Production

Electricity is generated in an alternator by rotating an assembly of conducting coils in a magnetic field. The coils, mounted on a shaft called a rotor, comprise the armature. The magnetic field is formed by a series of electromagnets energized by direct current supplied from an external source. The coils terminate in slip rings from which current is drawn through carbon brushes into the load circuit.

In a very simple case there might be two magnetic poles, North and South, and a single coil of wire. If this were rotated once in the magnetic field with constant angular velocity, the e.m.f. developed on open circuit (or the current through a constant load) would rise to a maximum, fall to zero and then to a minimum and then rise to the original value as the coil returned to its initial position, the graph of voltage against time t describing a sine curve, $V = V_m \sin \omega t$ (Fig. 3 (a)). This would correspond to one electrical cycle.

If there were four poles, North, South, North, South, one revolution of the coil would complete two electrical cycles, and so on. Further, if there were two pairs of equally spaced poles, two coils could be used, set at 90° to each other, and these would augment each other insofar as twice the current could be supplied. In such a case there would be a lot of space on the rotor not occupied by coils and other pairs of coils could be accommodated. If two more pairs were built on to the rotor at 30°, 120°, 60° and

150°, the original pair being at 0° and 90°, a three-phase supply would be obtained. Each set of coils would have its own pair of slip rings and, assuming the connections to these were made in a symmetrical manner, the timing of the electrical cycles of the three phases would be different from one to the next by one-third of a cycle. In electrical parlance the phases are displaced by 120°. See Fig. 3 (a).

In practice three-phase generation is the rule. The number of poles may be much higher than four and the magnetic field usually rotates with the rotor and the conducting coils are built into the stator. This simplifies the slip-ring problems. There are many detailed variations on this scheme but these need not be considered here.

The alternator is driven at such a speed as will give exactly 50 electrical cycles per second, and this is the frequency of the supply, 50 cycles (in the United Kingdom). The efficiency of conversion of mechanical energy to electrical energy is a function of alternator design and engineering and metallurgical skill in achieving what has been designed. The clearance between the rotor and the stator must be very small and constant. The coils are wound not on a solid former but on an armature core built up of hundreds of thin plates of iron insulated from one another with thin paper so that the coils and not the core carry the current. Overall conversion efficiency has increased in recent years from about 20 per cent pre-war to about 38 per cent now. Generators have increased in size at the same time from about 30 MW to 500 MW capacity.

Direct current can be produced in a similar device but the slip-rings are segmented so that current can be drawn only when it is flowing in one direction. This part is known as the commutator. Change-over from a.c. to d.c. or from one frequency to another can be effected by motor-generator sets in which the supply available is used to drive a motor coupled to a generator which has characteristics suitable for producing the kind of supply required.

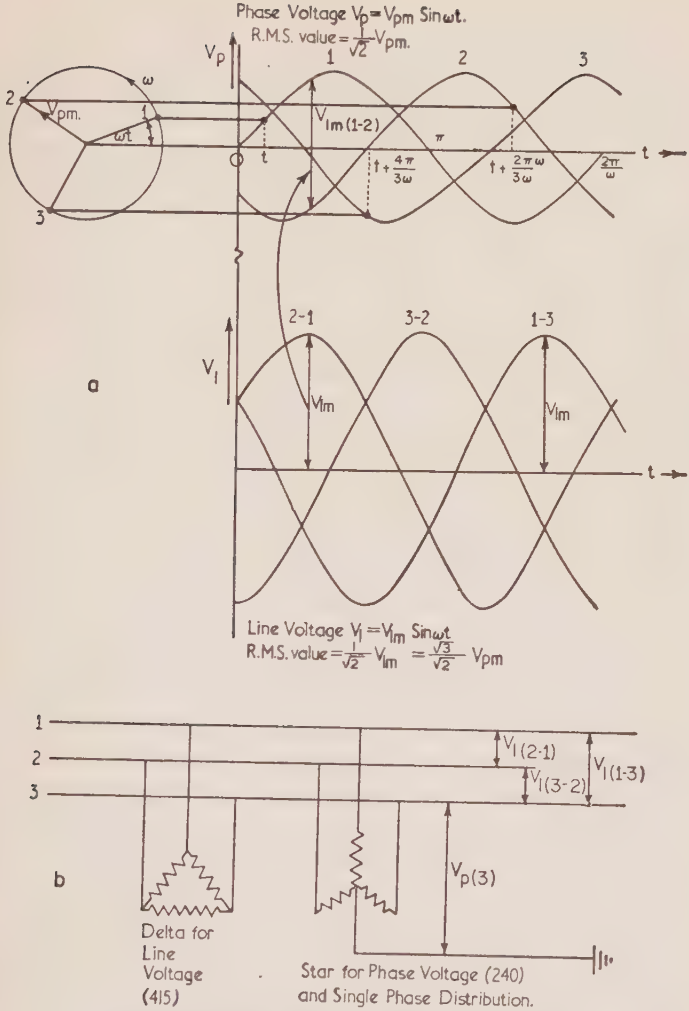
Phase Voltage $V_p = V_{pm} \sin\omega t$.
R.M.S. value $= \frac{1}{\sqrt{2}} V_{pm}$.
V_p
1
2
3
ω
V_{pm}
ωt
$V_{lm(1-2)}$
0
t
π
$t + \frac{4\pi}{3\omega}$
$t + \frac{2\pi\omega}{3\omega}$
$\frac{2\pi}{\omega}$
t
a
2-1
3-2
1-3
V_l
V_{lm}
V_{lm}
t
Line Voltage $V_l = V_{lm} \sin\omega t$
R.M.S. value $= \frac{1}{\sqrt{2}} V_{lm} = \frac{\sqrt{3}}{\sqrt{2}} V_{pm}$
1
2
3
$V_{l(2\text{-}1)}$
$V_{l(3\text{-}2)}$
$V_{l(1\text{-}3)}$
b
$V_{p(3)}$
Delta for Line Voltage (415)
Star for Phase Voltage (240) and Single Phase Distribution.

FIG. 3. Three-phase production and distribution of electricity. (a) shows the relationship between the phases and that between phase and line voltages, (b) shows how delta and star connections are made at distribution points.

Distribution

Electricity for general distribution is generated at about 12,000–20,000 V a.c. For distribution this is transformed up to one of the standard transmission voltages—265 kV on the national super-grid, 132 kV on the national grid, and 66 kV or 33 kV for regional distribution (in the United Kingdom). Tappings from the grid system are transformed down by stages for local distribution and voltages of 240 and 415 are ultimately available in the home and the factory for general purposes.

The three phases must be kept in balance and except for domestic users three-phase supply is the rule rather than the exception, and the consumer is expected to load them equally and keep them in phase. The phases are interconnected for transmission either by Delta (mesh) or Star (Y) connections as shown in Fig. 3 (b). In each of these any two wires are continuously acting as the return for the third, but domestic distribution uses a fourth wire connected at the pole of the Star at the sub-station transformer, at essentially earth potential. The normal voltage between line and this "neutral" wire is 240 (phase voltage), while that between phases in the Delta arrangement is 415 (line voltage). This provides a very good reason for maintaining single-phase supply in homes. Balancing the phases in domestic circuits is done statistically.

240 V single-phase supply is used for all domestic heating, lighting and power, and in laboratories most equipment up to 3 kW can be run off this supply. Industrial equipment involving heavy motors—lathes and other tools for example—would require three-phase, 415 V supply and be designed to use it. Industrial electric furnaces would require to be supplied off the three-phases, but usually at lower voltages so that the current and therefore the heating effect would be as high as practicable. Transforming down to low voltages is done near the furnace so that the heavy conductors required for the high currents will be short.

It will be realized that (at equal energy flow rate) a rise in voltage is accompanied by a proportional fall in current and therefore in transmission losses. Low-voltage high-current transmission requires bus bar connections to be very heavy, otherwise they will melt. The choice of 240 V for domestic supply in Britain is a compromise between lethal voltages and incendiary amperages.

Considering a single phase, if a voltage is applied across a load which has neither inductance nor capacitance the current which flows will be proportional to voltage at any instant and will therefore vary sinusoidally in phase with voltage. At any instant Ohm's Law is being obeyed and Watts = Volts × Amps. Integrating over a whole cycle the effective volts is the root mean square (RMS) value or 0·707 ($1/\sqrt{2}$) of the maximum or peak volts, and the effective amps during the cycle is 0·707 of the maximum amps so that the watts dissipated equals $\frac{1}{2}$ × Peak Volts and Peak Amps.

Alternating current meters measure RMS values of volts and amps, so that in non-inductive circuits the formula can be used that Watts = Volts × Amps (the indicated values).

In inductive circuits, however, the current continues to vary sinusoidally, but not simultaneously with voltage—a little behind, a fraction of a cycle expressed as so many degrees lag (where a degree is 1/360 cycle). Volts and amps are said to be out of phase and where θ is the angle of lag, power becomes Volts × Amps × Cos θ.

If a circuit has capacitance the amps may be in advance of volts by an angle θ with the same effect that power = Volts × Amps × Cos θ is less than it would be in the circuit with no inductance or capacitance. Cos θ is known as the power factor (p.f.) and depends on inductance and capacitance taken together.

As power is measured and charged as KVA and energy is usefully dissipated as KVA × p.f., it is highly desirable that the power factor be kept as high as possible and where necessary capacitance is introduced deliberately to advance the current so that the inductance in the load will retard it only to the optimum position—in phase with voltage. Most large electric furnaces require such capacitance banks to be installed.

Big industrial consumers frequently produce at least a part of their own requirements. This may be to effect economic use of waste heat or excess gas from their major operations and it is of some benefit in ensuring safety in the case of grid failures and in making some provision for peak loading periods. The tariff rates to industrial consumers vary with the type of equipment operated and in some cases are proportional to the rate at which power could be consumed on the grounds that so much generating capacity has to be available at all times. In cases like this, e.g. electric melting furnaces, the use of electrical energy can be justified only if the operation is continuous, round the clock. Lower rates may be available for power consumed overnight.

Electricity is used in three principal types of furnace—resistance, arc and induction furnaces. Resistance furnaces are in most general use in many industries at low and moderate temperatures. They provide excellent uniform heating and essentially "muffle" conditions without the disadvantage of a refractory screen interposed between the heating elements and the stock. Arc furnaces are used mainly by the steelmakers and particularly by manufacturers of expensive high-alloy steels. Induction furnaces are used for melting special steels and other alloys such as brasses and nickel alloys, and can be applied to very high-class work such as vacuum melting. Electricity is also used in a few specialized metallurgical extraction techniques. Generally in Britain the cost of electricity is too high to justify its replacing fuel except where some distinct technological advantage is to be gained, as in the cases of the high-alloy steels mentioned where only electric furnaces can be operated under the neutral or reducing conditions necessary for attaining the desired quality. Electricity is very easily controlled: it makes very high temperatures very readily attainable; and it is very clean to use particularly insofar as it produces neither sulphur nor ash at the point of use. There is at present a clear trend toward its extended use in steelmaking. The normal size of arc furnaces has rather suddenly inceeased and whole melting shops have been converted from gas-fired to electric arc furnaces for the manufacture of a wider range of steels than has hitherto been made in these furnaces.

9. Trends in Fuel Utilization

In Fig. 4 an attempt has been made to summarize present-day usage of fuel and power in Great Britain. The figures in millions of equivalent coal tons allow direct comparison of the energy supply or demand at each point. The iron and steel industry has been dealt with in some detail but the information given about other industries is not so complete. The overall picture is, however, fairly clear.

Over 80 per cent of our total energy requirements are met (1960) with coal or its derivatives and the remainder almost entirely with oil. Only 0·2 per cent comes from water and atomic power together. One-quarter of the coal goes to power stations to be converted with rather low average efficiency into electricity. A second quarter is carbonized or gasified. Most of a third quarter is used directly in homes and commercial premises providing comfort, cooking, and hot baths. The rest is consumed by industry.

Of the oil imported almost half is accounted for by petrol, derv and bunker oils, providing locomotive power on land, sea and in the air. Otherwise the largest consumers are the electricity industry and the steel industry while the central heating of domestic and commercial premises probably consumes about as much as the steel industry. The remainder goes to petro-chemicals, the heavy chemicals and other industries as a fuel, and to the gas industry.

It should be appreciated further that that half of the fuel which was delivered to the coke, gas and electricity industries is distributed after conversion and that those consumers who have

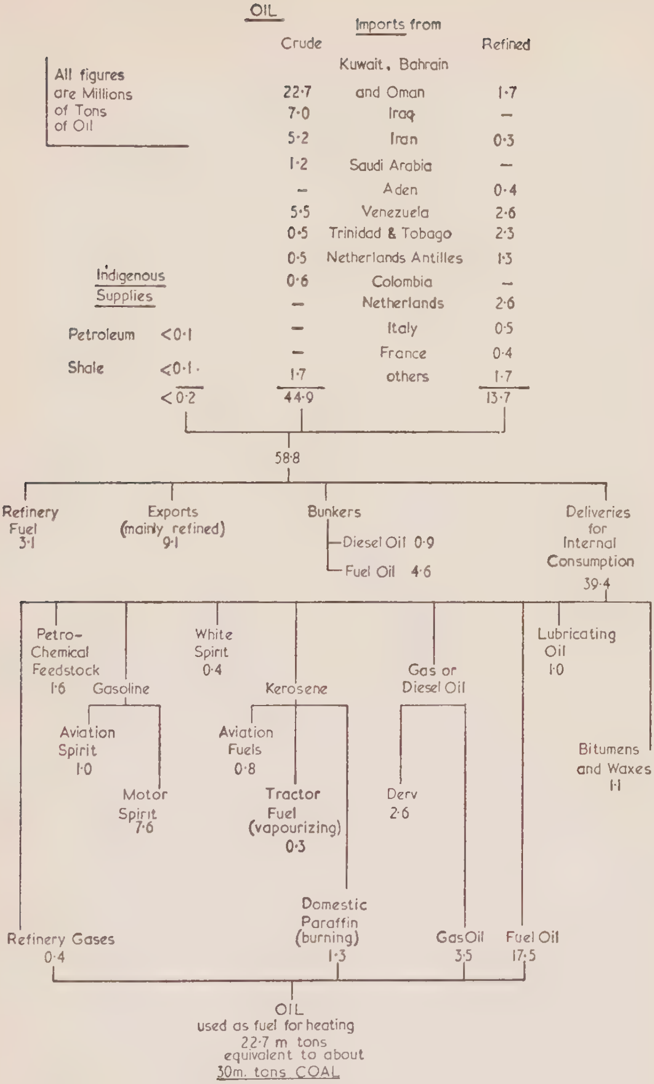
OIL
Imports from
Crude
Refined
All figures are Millions of Tons of Oil
22·7 Kuwait, Bahrain and Oman 1·7
7·0 Iraq —
5·2 Iran 0·3
1·2 Saudi Arabia —
— Aden 0·4
5·5 Venezuela 2·6
0·5 Trinidad & Tobago 2·3
0·5 Netherlands Antilles 1·3
0·6 Colombia —
— Netherlands 2·6
— Italy 0·5
— France 0·4
1·7 others 1·7
44·9
13·7
Indigenous Supplies
Petroleum <0·1
Shale <0·1
<0·2
58·8
Refinery Fuel 3·1
Exports (mainly refined) 9·1
Bunkers
Diesel Oil 0·9
Fuel Oil 4·6
Deliveries for Internal Consumption 39·4
Petro-Chemical Feedstock 1·6
Gasoline
White Spirit 0·4
Kerosene
Gas or Diesel Oil
Lubricating Oil 1·0
Aviation Spirit 1·0
Motor Spirit 7·6
Aviation Fuels 0·8
Tractor Fuel (vapourizing) 0·3
Derv 2·6
Bitumens and Waxes 1·1
Domestic Paraffin (burning) 1·3
Refinery Gases 0·4
Gas Oil 3·5
Fuel Oil 17·5
OIL used as fuel for heating 22·7 m tons equivalent to about 30m. tons COAL

FIG. 4—PART I

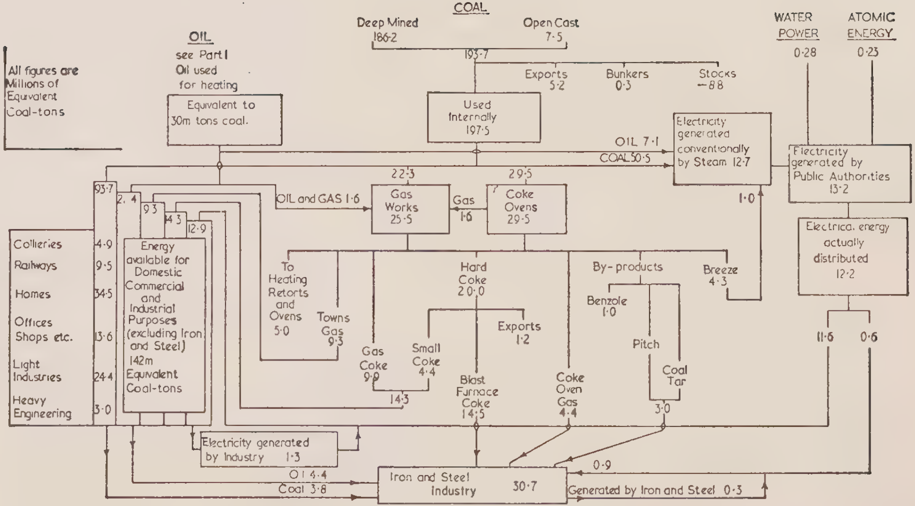
All figures are Millions of Equivalent Coal-tons
OIL
see Part I
Oil used for heating
Equivalent to 30m tons coal.
COAL
Deep Mined 186·2
Open Cast 7·5
193·7
Exports 5·2
Bunkers 0·3
Stocks −8·8
Used Internally 197·5
WATER POWER 0·28
ATOMIC ENERGY 0·23
OIL 7·1
COAL 50·5
Electricity generated conventionally by Steam 12·7
Electricity generated by Public Authorities 13·2
Electrical energy actually distributed 12·2
11·6
0·6
22·3
29·5
OIL and GAS 1·6
Gas Works 25·5
Gas 1·6
Coke Ovens 29·5
1·0
To Heating Retorts and Ovens 5·0
Towns Gas 9·3
Gas Coke 9·9
Small Coke 4·4
14·3
Hard Coke 20·0
Exports 1·2
Blast Furnace Coke 14·5
Coke Oven Gas 4·4
By-products
Benzole 1·0
Pitch
Coal Tar
3·0
Breeze 4·3
93·7
2.4
9·3
14·3
12·9
Collieries 4·9
Railways 9·5
Homes 34·5
Offices Shops etc. 13·6
Light Industries 24·4
Heavy Engineering 3·0
Energy available for Domestic Commercial and Industrial Purposes (excluding Iron and Steel) 142m Equivalent Coal-tons
Electricity generated by Industry 1·3
Oil 4·4
Coal 3·8
Iron and Steel Industry 30·7
0·9
Generated by Iron and Steel 0·3

Fig. 4—Part II

already been noted as taking large shares of coal and oil direct also require a lot of these secondary fuels. Homes, for example, use a high proportion of the town's gas, coke and electricity.

Fig. 5 indicates some of the trends in fuel usage in the past few years, going back to 1938 where possible. The changes in the pattern are not easily explained, there being so many factors, including weather, interacting with each other. Over the period examined the demand for energy has undoubtedly increased. National prosperity has increased. Productivity has risen rapidly except in the last two years. Standards of comfort and amenity have increased enormously. At the same time, however, there has been a great awareness that fuel costs money and very substantial improvements in efficiency of utilization have been made. New plant of almost any kind from a domestic fireplace to a power station is more efficient than old plant, and each time a change-over is made a saving of fuel per unit of production is certainly effected and often a saving of fuel in absolute terms, too. This applies to power-driven equipment as well as to furnaces. An electrically driven lathe or mill taking power from (in principle) a new efficient power station uses less energy than an old

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FIG. 4. The sources, production and distribution of the main forms of fuel and energy in Great Britain in 1960.

Part 1. The sources of supply of oil and its distribution as various products, of which almost 40 per cent is for heating purposes and is passed on to Part 2.

Part 2. Shows how coal and oil together supply the nation's needs of solid, liquid and gaseous fuels and of electrical energy and gives particular prominence to the requirements of the iron and steel industry.

Notes: Information is based on the annual Statistical Digests of the Ministry of Fuel and Power.

In converting all quantities to coal ton equivalents the following factors have been used:

1 ton coal $\equiv$ 0·935 ton coke.
$\equiv$ 0·75 ton oil.
$\equiv$ 312 therms.
$\equiv$ 9150 kWh.

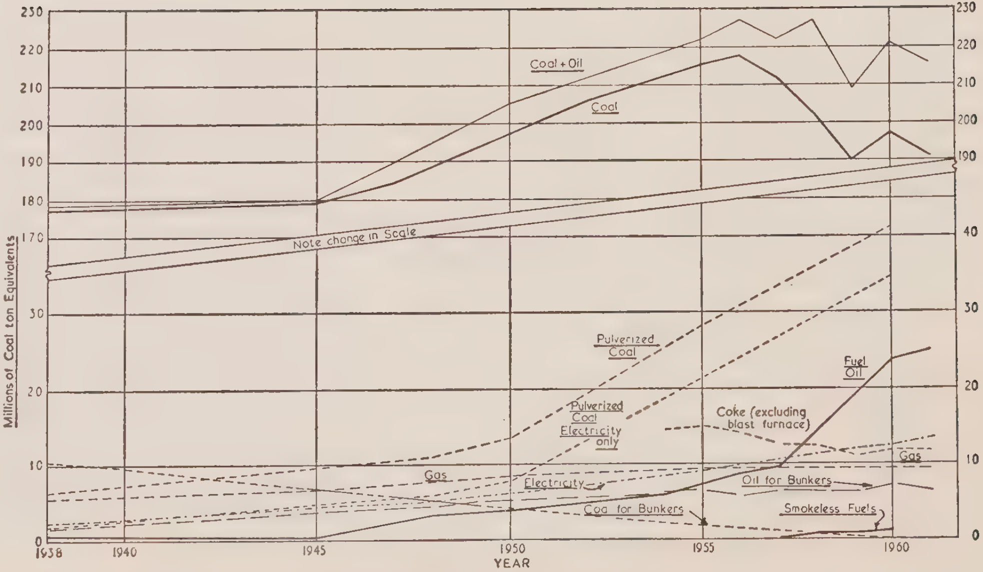

FIG. 5. The trends in Great Britain in the consumption of fuel and energy in various forms 1938–1961.

lathe powered perhaps by an elderly steam engine, shafts and belts, with an overall efficiency of only a few per cent. Similarly a diesel or electric locomotive uses less calories per journey than its steam-powered predecessor and the modern family car goes somewhat further on a gallon of petrol than its pre-war counterpart.

There is therefore a demand for more energy coupled with an increase in the proportion of the energy in fuel which is actually used. The rate of increase of fuel consumption is therefore less than that of energy demand, and there is no reason why at some stage an increased demand for energy may not be met by a reduced consumption of fuel.

The rate at which efficiency increases cannot readily be measured outside a few restricted industries. The improved efficiency of power stations has already been mentioned (p. 64), and is such that if the efficiency of 1939 had not been improved upon, our present output of electricity would be costing us about 20 million more tons of coal per annum than it actually does. Similarly the improvement in thermal efficiency of iron blast-furnaces since 1939 is saving about 3 million tons of coal each year. In each of these cases there is a big saving also on the cost of capital equipment—fewer power stations and coke-ovens being required.

Further great improvements are possible. In the generation of electricity the present "best" of 38 per cent is still appreciably short of the 45 per cent which is theoretically possible but in ironmaking the limit is being approached so closely that further improvement over best practice could only be achieved at considerable cost in other directions. Until this limit is approached by consumers as a whole improved efficiency affords the most satisfactory means of meeting increased demands for energy. When sufficient improvement is not being achieved extra energy must be obtained by digging more coal, importing more oil, or developing other supplies of energy such as nuclear energy. The present choice is still mainly between coal and oil but nuclear power will play a significant part in the next few years. It is, of course, highly desirable that the imported commodity shall be used where there is the greatest technological advantage and that it shall thereby release coal for use where it too is more appropriate.

The present overall trend as indicated by Fig. 5 appears to be that oil is capturing an increasing part of the coal market. The total amount of energy used per annum is nearly constant in the last few years, while the amount obtained from coal falls and that from oil rises. It should be remembered, however, that improvements in efficiency probably affect the utilization of coal more than that of oil and where a change-over is made from coal to oil there should usually be a net saving.

The biggest increases in oil consumption are in shipping, electricity and steel. In shipping the advantages of oil over coal are overwhelming and obvious. Refuelling is speeded up; space is released for cargo as oil can be stowed in places remote from the engine room, and the conditions in the engine room are immeasurably improved. Many ships are now powered by diesel engines. The loss to the coal trade of the bunkering business is permanent and not to be regretted. The use of oil in the electricity and steel industries followed coal shortages in early post-war years. There seems little reason why the proportion of oil used should continue to increase in the electricity industry in the face of reduced overall demand for coal, though plant designed to use oil must obviously continue to do so, and some new plant required to operate far from coalfields might reasonably be built to use oil. In fact, most oil-burning plant is in the London area. The present policy, however, seems to be to build bigger and bigger power stations in the coalfields and the siting of one of the biggest at Blyth in Northumberland, until recently one of the largest coal-exporting ports, seems very appropriate to modern conditions.

In the steel industry oil-firing techniques probably have had much more care lavished on their technical development than the traditional gas-firing ever had, and oil is now generally believed to give faster production rates than gas-firing and therefore to be economically preferable. It is almost certainly true that oil gives better results than lean producer gas in open-hearth furnaces, but its advantage over coke-oven gas cannot be very great. Figure 4 suggests that there is no coke-oven gas to spare at present, but the question is whether more rich gas should not be made from coal for the purpose rather than more oil imported. In other countries natural gas is used for this purpose and methane from coal measures in Britain could be so used instead of being mixed in with leaner gas for general distribution. In the same way the recent development of oil injection in blast furnaces could equally well be injection of a rich gas like coke-oven gas if there were supplies to spare.

In the steel industry other developments are afoot, however. The proportion of steel made in electric arc furnaces is increasing significantly and these derive their energy largely from coal. Secondly the new "L–D" and "Kaldo" processes, developments of the basic Bessemer process, are coming into favour for the cheaper grades of steel. In these the fuel used is ultimately in the form of blast-furnace coke so that even in the steel industry the trend is not running all one way.

The railways, too, which have gone a long way toward replacing coal by oil are expected to change over to electric traction in the next 10 or 20 years—again reverting to coal, unless by that time nuclear energy is playing a major part in electricity production.

It is on the domestic front, in commercial premises, and in light industry that the battle between coal and oil appears to rage most fiercely. In spite of the great improvements that have been made in the design of all sorts of stoves, fireplaces, stokers and other appliances for burning coal it seems likely that the use of raw coal will gradually dwindle to almost negligible proportions. At present the coal-traders are advertising their wares for the first time and introducing such commercial gimmicks as fancy packaging and slot-machine vending, but the rigours of clean air legislation must eventually make the use of raw coal very difficult.

Most coal merchants are now "solid fuel specialists", however, and sales of coke and other solid smokeless fuels are already increasing rapidly. At present many of these have the disadvantage of low density, which affects the effective capacity of both the bunker and the grate. These fuels are also rather expensive largely because of transport costs from areas where there are coals suitable for their manufacture. Efforts are being made to develop denser smokeless fuels and to make them from a wider range of coals.

For many purposes gas is more appropriate than a solid fuel and it seems likely that it is in this form that a high proportion of coal will eventually reach the public, possibly at a higher calorific value than at present to make it more directly competitive with oil. There is often little to choose between gas and oil except when extremely intense heat is required. The choice is often made on the basis of current prices (which are not easy to compare) and convenience in use (where they are potentially equal). Both are on tap at the point of use and can be arranged for a high degree of automatic control. Oil requires local storage capacity whereas gas is piped and may be found to be at low pressure when requirement is greatest. Neither should cause any smoke, smell or ash. Oil is inherently cheaper (per calorie), but is more liable to be adjusted upward by taxation or by political events in the producing countries.

On balance, oil probably has the advantage of price, but no advantage technologically and a potential disadvantage strategically. That the curve for gas consumption in Fig. 5 remains almost horizontal indicates that insofar as the consumption of raw coal is falling in smokeless zones and elsewhere it is not yet the gas industry that is benefiting but rather the smokeless fuel industry and the oil industry.

For many purposes gas and oil are in competition with electricity. This is by far the cleanest, most convenient, most versatile of all forms of energy, and there is an obvious trend in the affluent society of today to buy convenience even if it is rather expensive. Electricity is the most expensive form of energy (per calorie), but it is the most efficient in use, the inefficiencies having occurred at the power station and being reflected in the price. As with gas, complete continuity of supply cannot be assured and the vastly increased demand of recent years has put the distribution networks under great strain but the frequency of power failures is low and their duration short. The occasional inconvenience caused by them sometimes does, however, necessitate the installation of stand-by equipment. Electricity is, of course, a source of light and power as well as of heat and is now used by nearly everyone in the country.

As Fig. 5 shows, the increase in consumption of electricity is rapid and continuing. This necessitates vast capital outlay on plant and distribution networks and if demand should continue to rise to the point where everyone is using as much as the wealthier section of the community does today, the problems of maintaining the service in terms even of space required for equipment will become difficult to solve. The present work on super grids and the plans laid for even higher voltage transmission are a start toward meeting these problems. In the distribution of both gas and electricity the problem of meeting fluctuating demand on both a diurnal and a seasonal basis, economically, is being tackled in various ways. Electrical linkages with other countries is one move to help with the problem. Old inefficient plant is being reserved for peak load supply only and hydro-electric power, too, is used for peak load supply as far as possible. Efficiently produced power is being used by night to pump water to high reservoirs for use again during peak loading times when the alternative would be to build more generating plant which would then have to lie idle all night and most of the day. Developments like these should make electricity relatively cheaper—and presumably cause even further increases in demand.

Only limited further extension of our hydro-electric power industry seems now possible but the expansion of nuclear power programmes goes on in Britain and other economically and technically advanced countries. To date, electricity made from nuclear energy is rather dearer than that made from coal and steam but the industry is still in its infancy and is developing fast. There is no certainty that it will ever make cheaper electricity than conventional plant, but as long as the difference is not great, that is no reason why the development of nuclear power stations should not continue. In the long run an alternative source of energy will be needed. These nuclear power plants may also be useful in underdeveloped countries if they can be designed to be used without too big a force of highly skilled labour in attendance. One small plant already operates in Antarctica under the supervision of United States Army personnel. In most underdeveloped countries it would seem that the development of water power is more appropriate at this stage than nuclear power.

It would appear that known reserves of the major forms of fuel are high and ample to keep mankind warm and busy at his present rate of use for many centuries. Special kinds of coal may be in (relatively) short supply but British reserves of coal alone appear to be enough for about 800 years at our already high rate of consumption. The coal may not be easily won, but it is there. On a population basis, other countries are much less well endowed, but most major centres of population are near to supplies for at least half that time. Major industrial communities have, of course, grown up around the coalfields of Europe and America, and in these areas living standards are highest and coal is being used up fastest, but other countries like China, Russia and India have coal to supply themselves at much greater rates than at present for a long time to come.

Reserves of petroleum are not so spectacular. Indeed the total known reserves appear to be enough for only some 30 years or so. New reserves are being discovered, however, faster than the old ones are being consumed and the reserves of oil in shales and oil sands are even greater than those of petroleum and are as yet untouched. It is not unlikely, however, that the structure of the oil industry may have to change to meet changing circumstances of supply whether for geological or political reasons from time to time and oil may well fail to survive the twenty-first century as a major primary fuel.

The probable requirements of uranium for the development of nuclear power can hardly be guessed but if 1 lb of uranium is equivalent to 1000 tons of coal, 100 tons would replace all Britain's coal for a year. Breeder techniques would allow this fuel to go even further. Uranium supplies have turned out to be much more plentiful than had been believed some ten or fifteen years ago. The successful harnessing of the energy of fusion of the light elements into heavier ones would of course solve all the long-term problems for all time but the answer to this one is not yet with us.

Reserves of water power and tidal energy are of course replenishable and, short of a new era of glaciation, everlasting. Wood, too, is replenishable but at a limited rate. The heat in the sun and in the core of the earth are also inexhaustible sources of supply which can be tapped, so that ample heat and power in some form and at some price will always be available as long as man's will to bend the resources of nature to his purposes persists.

PART TWO

Refractories

10. Classification of Refractories

There is no general definition of a refractory. Essentially it is a material of "high melting point", but this is a relative term and melting point is not the only criterion of usefulness.

Most refractories are ceramic materials made from high-melting-point oxides, particularly SiO_2, Al_2O_3 and MgO. Carbon is now an important refractory, however, and carbides, borides and nitrides are also being developed for high-temperature work. Metals like Mo and W are refractory metals and find uses in research apparatus. Even these may be melted in heavily water-cooled copper containers which, if not classified as refractories, certainly replace them.

Finally there are materials like asbestos which have not a high melting point, but which are used as medium or low-temperature insulation and should not be excluded from consideration.

Refractories may be classified by chemical composition and in this book the broad division is into those based on silica, alumina and silica together, and magnesia and chromite either separately or together. This leaves a residue, much of which can be incorporated into the most usual classification which depends on behaviour toward metallurgical slags as follows:

Acid refractories are based on SiO_2 and include silica, and the fireclay series with 30–42 per cent Al_2O_3, sillimanite and andalusite with about 60 per cent Al_2O_3.

Basic refractories are based on MgO and include magnesite and dolomite, chrome magnesite and magnesite chrome. In addition alumina and mullite bricks are classed as basic and many "special" refractories like ThO_2 and BeO would come into the same category.

Acid refractories react readily with basic slags and basic refractories are attacked by acid slags as a general rule.

Neutral refractories would be relatively inert to both siliceous and limy slags and this class includes carbon, chromite ($FeO.Cr_2O_3$) and forsterite ($2MgO.SiO_2$) bricks.

"*Special*" refractories are usually new, or very expensive materials, such as the ZrO_2 and BeO mentioned above, and are reserved for research purposes, and other occasional uses such as in atomic energy and gas turbine technologies. These could also be classed as acid, basic or neutral, but this classification would not have any great practical significance. The term super-refractory is now being used for some of these materials whose melting points lie above about 1900°C.

For industrial use refractories are largely marketed as bricks of a variety of standard shapes and sizes or in non-standard sizes at somewhat higher cost. There are many standard shapes including tapered bricks to facilitate the construction of curved walls and arched roofs free of gaps between the bricks. Other standard shapes such as tubular sleeves for stopper rods have very specialized uses. Some materials are supplied in granular form often described as "pea sized" and this is built into a furnace while it is very hot by throwing thin layers on to the hearth and letting these frit into position. The same preparations, mixed with hot tar as a binder, are used to line the hearths of new furnaces. Some refractories are made up as "castables"—plastic preparations which can be made up to any shape and are dried and fired *in situ*, and are useful for effecting running repairs. For every kind of brick there should be a cement of similar chemical characteristics but preferably of plastic consistency. They may be made up suitably tempered with water and possibly other additions or may be supplied dry for preparation on the building site.

Laboratory ware and research equipment are available in the forms of crucibles and tubes with other shapes to special order.

These articles may be porous or impermeable and gas-tight. The new and the unusual, special both with respect to material and shape, are frequently in demand for aircraft engine, atomic energy and rocketry purposes. For these purposes, however, pure substances and mixtures of pure substances are required and the term refractory is not good enough so that we find the materials here called "ceramics", the meaning of which is gradually being widened to include practically any non-metallic inorganic substance of high melting point.

11. Properties and Testing

Failing a definition of a refractory material, a discussion of the qualities sought in it is essential. The most important requirements of the user are:

1. Rigidity and maintenance of size, shape and strength at the operating temperature, which will presumably be "high".
2. An ability to withstand thermal shock such as is met in heating up and cooling down of furnaces, or in fluctuations which occur during charging or during normal operation.
3. Resistance to chemical attack by whatever gas, slag or metal is likely to be encountered.

As there is no supreme material capable of standing up to every possible condition, the choice must be made to meet the requirements of the job to be done. Compromise is usually necessary. Other properties such as cold crushing strength, and thermal conductivity are usually of secondary importance but occasionally, as in insulating bricks, one of these may become of prime importance. The properties actually measured are sometimes only an indirect guide to quality and must be interpreted with care. Thus high porosity will lead, *aliter parsim*, to reduced slag resistance and lower thermal conductivity, and this latter in turn to poorer spalling resistance. But higher porosity may be achieved by lower firing temperature resulting in less vitrification which in turn leads to high permeability (worsening slag resistance) but alters the mechanical strength to improve spalling resistance. Empirical tests have been developed—some of them not very satisfactory—for slagging, spalling, etc., which are intended to be a more direct guide to behaviour than fundamental measurements. The following tests are commonly carried out. B.S. Specifications are available for some of them marked * and details can be found in B.S.S. 1902 (1952), or in an appendix to "Steel Plant Refractories".[9] A similar series of tests is specified by the American Society for Testing Materials.

1. *Visual examination* should indicate general uniformity, vitrification, texture, etc. This is obviously a job for an experienced eye, but variations within a batch or between batches which are obvious are probably significant.

2. *Dimensional accuracy* is important when large structures are to be built. A ruler or calipers would be used. Edges should be straight and free of chips. Faces should be flat. Tolerances demanded can be very small indeed because, of course, the furnace has to be the correct shape and size when the requisite number of bricks are placed together. If the shape is good and the faces flat, bricks can be set dry, i.e. without using cement.

3. *After expansion* (or contraction)* is easily determined by heating a suitable sample of bricks for a prolonged time at the proposed working temperature. The bricks (or cut samples) are measured before and after treatment to determine the permanent change in dimensions which should, of course, usually be very small. The test must be related to working conditions. If the expansion (usually a contraction) is too great, more thorough firing is required, or another kind of brick. High values lead to severe cracking of furnace walls during use, or to distortion of the structure. A small expansion is preferred, to give tight joints, and for some special purposes like ladle linings a fairly high value is deliberately arranged.

4. *Reversible thermal expansion** is determined versus fused silica (whose coefficient of expansion is very small) in any standard type of dilatometer. Here one is determining the coefficient of thermal expansion along with any volume changes due to polymorphic transformations. The latter may give evidence of imperfect firing

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[9] *see* bibliography.

(e.g. in silica). The expansion is a necessary design datum as it must be accommodated as the furnace heats and cools during operation. It is also related to spalling resistance, and a low value is desirable on all accounts, but every type of brick has its own characteristic behaviour in this respect, and in some cases, e.g. magnesite, an otherwise admirable brick may be difficult to use because the coefficient of expansion is inherently high (see Fig. 6).

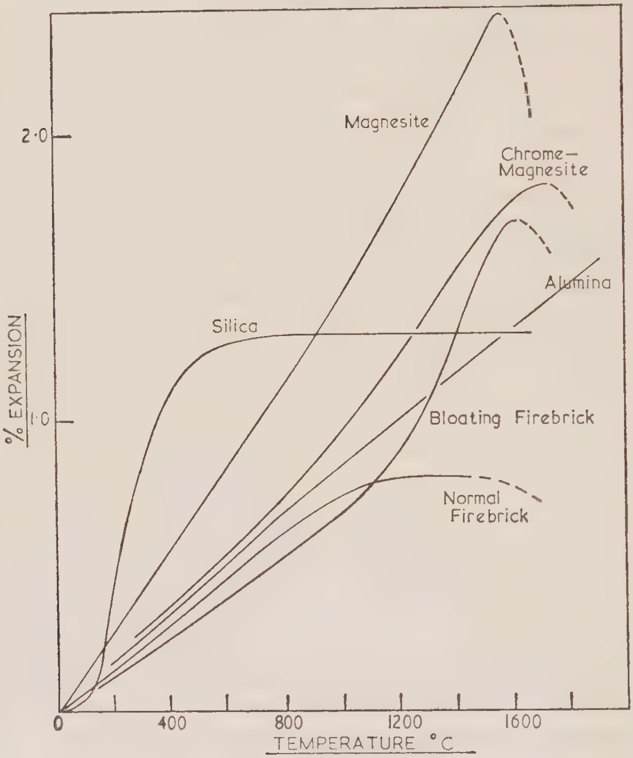

Fig. 6. Typical expansion curves for various refractories.

*Refractoriness.** It is not generally practicable to measure the melting point of a refractory. Usually melting extends over a range of temperature—perhaps over several hundreds of centigrade degrees. The determination of solidus and liquidus temperatures would not be easy and might not be very useful. A material may be partly liquid yet appear solid. At a higher temperature where the proportion of liquid exceeds a critical value which may depend on its viscosity, the material will either collapse and appear liquid or pasty, or will exude liquid and collapse slowly later. The apparent temperature of collapse may well depend on the rate of heating, particularly if the liquid is very viscous.

The test for refractoriness is to compare the sagging of a "cone" of the material (either cut from the solid or made up from powder and a bond of dextrin) with that of standard Seger cones, when they are heated together, at a standard rate in an oxidizing atmosphere, until the test cone bends over. The number of the best matching Seger cone is quoted as the refractoriness of the brick; or its nominal melting point (which can be checked by pyrometer) is referred to as the Pyrometric Cone Equivalent (P.C.E.) Temperature. As will be seen later, this is usually much higher than the working temperature of the brick. Refractoriness is a guide to quality rather than a measure of usefulness. The refractoriness of basic bricks is always very high and seldom quoted because such differences as there are beyond 1750°C are of no practical significance.

*Cold strength** is measured by a simple compression test called the Cold Crushing Strength test. It is seldom needed to assure the user that the brick will not fail in compression but results may be used to show whether or not the brick has been properly fired. The test might also indicate whether the brick would transport readily without damage to corners and edges.

Hot strength is very important in high-quality bricks but is not measured directly. Instead it is a temperature that is determined —that at which deformation under a standard load is rapid. The test is called the Refractoriness under Load* test (or R.U.L.), and is rather like a short time creep test.

A constant load of 100 or 200 lb (or 25 or 50 lb/in.^{2}) is applied to a prism of brick 2 in. square by 3½ in. high. The specimen is heated in a carbon granule furnace at a standard rate (10°/min) and a record of its height made, preferably by automatic plotting, until the test piece collapses or sinks to 90 per cent of its original length. The Refractoriness under Load may be quoted as the range of three temperatures:

(1) Initial softening (at which the curve is horizontal) (see Fig. 7).
(2) Rapid collapse (contraction rate 0·05 in./min).
(3) Total collapse (beyond 10 per cent shortening).

Sometimes the temperature at which shortening is 5 per cent is noted.

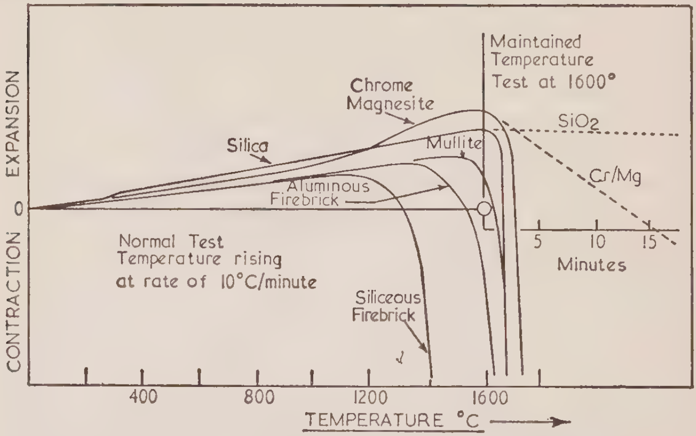

Fig. 7. Typical R.U.L. curves for various bricks. The behaviours of silica and chrome-magnesite under sustained load at 1600°C are compared in the inset.

A more satisfactory alternative is to stop heating at a suitable temperature, related to the working temperature, and to measure the creep rate during the next few hours. The object is of course to determine the maximum temperature at which the brick could be used under compressive load. It will be appreciated that usually not all of a brick would be at the hot-face temperature. The "cold" end would normally remain rigid even after the hot end had exceeded initial softening. The extension of the period of these severe conditions from hours to weeks is not readily predicted and leads to difficulty in correlating test results with practical performance.

Hot strength depends on the structure of the brick as well as on its melting characteristics and may persist beyond the solidus temperature if the major constituent has recrystallized during firing to form a three-dimensional network of interlocking crystals of high melting point which can maintain its rigidity even while a part of the material is molten in its interstices. The crystals of hexagonal tridymite and orthorhombic mullite behave in this desirable manner in acid refractories but the minerals in basic bricks usually have cubic habit and do not interlock, but, like glasses, deform slowly but continuously under load at high temperatures.

Other mechanical tests have been mentioned in the literature but are not in common use. Long-term creep testing would obviously be useful. The measurement of elastic constants has been reported as a check on thoroughness of firing. Abrasion tests using modified shot-blasting equipment have been described by Mackenzie[1] who successfully compared carbon and firebrick in favour of the former and observed that the most resistant part of the firebrick was its skin. Where bricks are to be subject to severe abrasion such a test is obviously worth trying though simple correlation with performance in the furnace may not always be obtained. Mackenzie noted a correlation between his test results and a transverse breaking stress determination which might afford a better measure of abrasion resistance and strength generally, at elevated temperature.

Thermal shock resistance is measured by a *Spalling Test.** There is no fully standardized test but materials can be compared using constant test conditions and these should be chosen to suit the brick under test and the working conditions under which it is to be used. For example, silica bricks have excellent thermal shock-resisting properties above 300°C if properly made, but shatter if cooled quickly below that. Any spalling test on silica must avoid cooling under 300°C. Similarly, a furnace would not be cooled below 300°C with silica in it. Various tests used involve heating either a brick (or several) or a prism cut from bricks, slowly up to a working temperature, and then cooling it rapidly for 10 min in a cold air jet, or on a steel plate, then reheating for 10 min in the furnace held at the working temperature. This is repeated until a piece of the brick becomes detached. The number of cycles to failure is noted. A brick surviving 30 cycles is claimed to be very good and quoted as having a spalling resistance of + 30 cycles. The size of sample and severity of the heating and cooling must affect the result, and are usually much worse than met in practice. In some tests only one end of the brick is heated and cooled which again exaggerates the temperature gradient. A more elaborate test involves building a small wall of the bricks and heating it with gas burners, and subsequently cooling with air blast. This would normally be designed to simulate some particular practice. In this case heating and cooling are applied to the face or end only and not along the sides as well.

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[1] J. Mackenzie, *Trans. Brit. Ceram. Soc.* 50, 1951, p. 145.

The result of a spalling test must depend on at least four properties of the brick—(1) its thermal conductivity which determines the temperature gradients set up under the test conditions; (2) the coefficient of thermal expansion which determines the strain induced by these thermal gradients; (3) the modulus of elasticity and (4) the shear strength of the brick substance which together determine the stresses set up and whether or not they will be relieved by crack formation or propagation. The formation of cracks during early cycles would probably modify the temperature distribution during the later cycles in favour of even more severe stresses so that cracks, once formed, are likely to get worse. The mechanical properties of the material depend in a complex manner on the chemical nature of the substance and on its crystallographic condition as well as on the general distribution of grains of mineral, bonding matrix and pore space, or, in more practical terms, strength depends on porosity, and in thoroughness of firing, and where appropriate on the distribution of "grog" particles which help to arrest cracks.

Slag resistance is also difficult to test other than qualitatively. There are three types of test. The most common involves drilling holes in the brick and packing these with samples of typical slag, likely to be encountered. The assembly is then heated to a working temperature for about an hour, cooled and sectioned. The extent of the penetration of slag into the brick is noted and compared with others.

The second method is to mix ground brick and ground slag in various proportions and to determine the melting points or refractoriness of the mixtures. A graph of melting point vs. per cent slag can be drawn and graphs for different bricks—or different slags—compared. The choice of slag is of course appropriate to working conditions.

This second test is a measure of the inherent reactivity of the substance of the brick to the slag in question. The former takes some account of the effect of brick texture and slag surface tension as they affect reaction rates. It is still rather severe, however. It provides a breach in the normally dense skin of the brick, and it employs a brick in which there is no temperature gradient—the cooling effect back from the face would normally slow up slag reaction.

The third type of test again tries to simulate practical conditions and either individual bricks are dipped in slag, or hot slag is sprayed on to hot walls built into specially designed furnaces. Field trials may incorporate panels of test bricks into working equipment for comparison with standard types.

The extent to which a given brick will be attacked by any particular slag depends first in the chemical reactions likely to take place between them, secondly on whether any of the products of reaction are liquid at the working temperature and thirdly on the speed with which the reactions are likely to proceed. Generally acid slags react with basic bricks and basic slags with acid bricks but this is an over-simplification. Iron oxide, for example, one of the more corrosive reagents, may occur in either acid or basic slags and can damage both acid and basic bricks—or be contained by either type of brick in suitable circumstances.

The behaviour of bricks versus slag can in principle be predicted from the appropriate thermal equilibrium phase diagram.

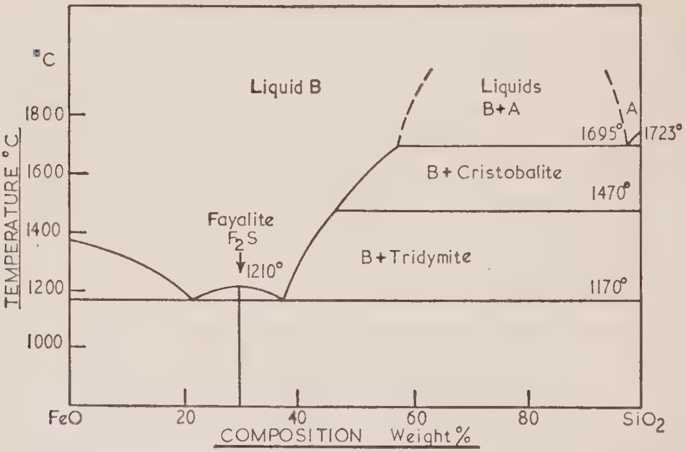

FIG. 8. The FeO–SiO_2 equilibrium diagram (after Bowen and Schairer).

Figure 8, for example, might be used to deduce that iron oxide would rapidly form a slag with a silica brick, and this could be confirmed by employing a test using the second method mentioned above. It is a matter of experience, however, that silica bricks stand up remarkably well to iron oxide attack presumably because the slag which forms at the face of the brick is very viscous and reduces the rate of attack to a very low value.

In most cases a ternary or higher order phase diagram would be necessary from which to determine probable slagging behaviour and very careful interpretation is usually needed. Two examples are discussed in the section on firebricks for which the appropriate systems have been investigated and phase diagrams published, but in many cases the diagrams have not yet been worked out in sufficient detail, especially when we consider that most refractories contain quite a lot of "impurities" which are often potential fluxes. Even where adequate information is available in the form of phase diagrams their interpretation is not simple. Phase diagrams describe equilibrium conditions but slag attack does not involve much equilibrium. A cursory inspection of the liquidus surface or a few isothermal sections is seldom sufficient. Appropriate vertical sections must be drawn and an effort then made to deduce the phases present between the unchanged brick and the unchanged slag after some sort of dynamic equilibrium or steady state condition has been set up, and to estimate the proportion of solid to liquid and the probable rheological properties of this mixture of phases (see page 114).

*True porosity** is a popular test on bricks and is generally considered to give a good index of quality. Its measurement involves the determination of real density and apparent density by standard methods.

Porosity is determined in the manufacturing stage by the size grading of the raw mineral, by the moulding pressure, and by the firing temperature and its duration, the effect of these last two being very much influenced by composition. Low porosity achieved by grading and moulding pressure is valuable in conferring high resistance to abrasion, to slagging, and to attack by gases such as occurs in the iron blast-furnace. Low porosity due to a high flux content and over-firing would not enhance the slag resistance but would probably give a very poor spalling resistance. Porosity values are usually about 20–25 per cent with lower values down to 12 or 15 per cent obtainable with some difficulty when thought to be desirable.

*Real density** is determined on crushed and ground material by the density bottle method. In firebricks the value obtained may reflect the degree of vitrification and in silica bricks it is used as a guide to completion of firing (see later), but generally the value is of little significance on its own.

*Apparent density** of porous materials is difficult to measure accurately. Evacuation in a vacuum desiccator and flooding with paraffin to fill the unsealed pore space, followed by weighing in air and in paraffin, is a common method. The value obtained is of little use unless perhaps to calculate loads for transport. The same data can be used to calculate *apparent porosity* or, in conjunction with real density, *true porosity*, including closed-pore volume. Recent demands for low-porosity bricks have led to values down near 10 per cent being achieved with difficulty. High resistances to abrasion and corrosion are thus obtained, and impermeability toward gases, but the spalling resistance is severely impaired.

*Permeability** is measured in a simple apparatus in which air is blown at a measured rate through a prism or cylinder of brick, the pressure drop being measured by a manometer. There seems to be little justification for the test except that, taken into conjunction with porosity, "texture" may be deduced—e.g. low porosity and high permeability may indicate cracks; high porosity and low permeability, closed pores or very small pores. Permeability may vary with direction through bricks made by the dry-press method, indicating stratification. Where reaction with gas is possible, low permeability is of course very desirable.

*Thermal conductivity** is usually measured on whole bricks. The apparatus used comprises a hot plate on which the brick sits on its largest face, with insulation round about designed to ensure parallel flow of heat out through the brick at least at the centre. On top is a brass plate to distribute temperature evenly, and in the centre a blackened copper disc insulated thermally from the plate, but in the same plane. The hot-face temperature, and that in the disc can be measured with fine thermocouples. Draught screens are erected round about and the temperature of still air over the assembly measured. The heat loss from the disc by radiation and convection is obtained by empirical formulae and the thermal conductivity calculated using the heat through-put and temperature gradient after equilibrium conditions have been established. At high temperatures more elaborate design is necessary to ensure parallel heat flow through the central section of the brick.

The value of thermal conductivity obtained is an effective conductivity insofar as the mode of heat transfer through the typical refractory with its 25 per cent porosity is only partly by conduction through the mineral grains and across the bond from one grain to the next. At high temperatures convection in the pore space and particularly radiation across the interstices become important. There is therefore a relationship between conductivity as measured and the structure or texture of a brick. The inherent thermal conductivity of the brick substance is the overriding factor determining the normal value for any type of brick and in this respect basic bricks will be found to differ significantly from acid bricks. Bricks of very high porosity are made when low conductivity is required (see Table 11).

*Chemical analysis** of refractories is carried out by standard classical methods, but spectrography or X-ray fluorescence techniques could be employed for some elements by manufacturers carrying out large numbers of analyses and special techniques like flame photometry for alkalies could be useful alternatives. Results of analyses indicate primarily the type of brick, e.g. the percentage alumina in a firebrick classifies it as siliceous, ordinary, aluminous, etc. Details of the analysis may also indicate the quality of the brick within its class, e.g. the level of alkalies and other potential fluxes has a strong effect on refractoriness of, say, aluminous firebricks. The overall analysis is not a complete description of quality, however, and especially in basic refractories the distribution of constituents is sometimes of much greater importance than their proportions.

Petrography. The petrographic microscope can be used on thin sections (one-thousandth of an inch) of brick to find the nature and distribution of minerals in the material. This can be applied either to the new brick or to follow changes occurring in firing or in service, or under attack by slags. Refractive index and isotropy are used to aid identification of minerals present.

Reflected light microscopy has also been used on polished sections but identification is dependent primarily on the petrographic technique.

X-ray diffraction can also be used to study mineralogical constitution and changes which may occur in firing or in service. The diffraction photograph would consist of series of "lines" for each mineral present above about 2 per cent and the system could be made semi-quantitative if necessary, but could not demonstrate spatial distribution.

12. Manufacture of Refractories

EACH kind of brick is made from a different raw material and its treatment usually involves some very special features, but there are so many common features that a consideration of the general principles will now be made.

Raw materials are mineral deposits—clays, sands, ores, rocks—which must be mined or quarried and then crushed. Many of these materials are imported, usually in bags to maintain purity, and some are very expensive. Fireclays are mined in this country and usually bricks are made at the mine head. Other types of brick are often made by the same companies in the same areas where coal is usually available and often the markets are handy also.

Crushing is carried out by simple ore-dressing equipment and material should be graded and stored by size.

The composition of the brick is adjusted by blending the materials along with any flux or bond additions that may be required. In many cases there is only one mineral used with appropriate bonds added. Blending is, however, not only by composition but also by size and the properties of the product depend very much on this stage. Low porosity can be attained by using a "close-packing grading" such that interstices between the largest particles are filled by a smaller grade, and residual interstices filled by a smaller grade again and so *ad infinitum.* Thus there is some control on the ultimate porosity—and on strength, for the maximum number of contacts will also be made with the closest packing. In basic bricks the coarse and fine fractions are sometimes of different composition and the fine fraction ultimately acts as the bond. "Grog", or prefired materials, may also be mixed in at this stage. This may consist of broken and crushed scrap brick but sometimes specially hard fired material is prepared for the purpose. "Chamotte" has long been used in Europe. Recently "synthetic mullite" grog has been produced in Britain, fired at 1750°C to assist in the manufacture of high-duty refractories of the mullite type with high abrasion resistance and low permeability to gases.

Blending is carried out in a paddle mill with a kneading action where addition of water and bonds (sometimes temporary) are added. Clays attain some plasticity at this stage. Other mixes remain friable.

The next stage is moulding. Standard shapes are machine moulded, non-standard shapes by hand. Hand-moulding is most successful with plastic mixes usually rather wet (14–20 per cent water), which can be "thrown" into the wooden box-type mould and relied on to fill it. It is cheaper than machine-moulding on a jobbing basis, but the machine is preferred, as usual, for mass production. Semi-plastic machine-moulding with about 10–12 per cent water uses moderate moulding pressures and usually a two-stage process—extrusion to a rough shape followed by pressing to an exact shape. The dry-press method is used for all the non-plastic basic mixes as well as clays with not more than 5 per cent of water. Mixing in so little water is not easy and usually a fine spray or mist is used. When high pressures of the order of 5000–20,000 lb/in. are applied in the mould, air is liable to be trapped and cause laminations. Because of this, clay may be deaired by vacuum treatment either before moulding or, better, using vacuum blocks in the mould wall. Green strength is rather low in these bricks so that it is difficult to maintain good edges and corners, and handling of the green bricks should be mechanical as far as possible.

The only other important forming process is slip-casting, applicable mainly to clays which can be formed into a colloidal suspension with water and poured into a mould of plaster of

Paris which absorbs the water and causes a uniform deposit of clay to build up in the inside of the mould. This is obviously most useful for awkward shapes and for hollow ware. It is also used for special refractories which are prepared from very fine powders.

The bricks must then be dried. This is conducted either on large drying floors (heated by waste heat from kilns) where the bricks are laid out in open array, or in tunnel kilns where they are stacked on bogeys and passed through a tunnel against a stream of hot air. This is the faster and more compact process but cannot readily be adopted where sizes and shapes are not fairly constant.

The final stage is firing. The traditional furnace was the beehive kiln but this has been superseded by numerous developments. In one case there are a large number of kilns side by side. The firing kiln at any time is heated by a fire of coal or coke, using air preheated by being drawn through several cooling kilns. The combustion products are passed over bricks in several preheating kilns before passing to the stack. Heating must be uniform in each kiln so that the bricks attain a uniform temperature before the fire is advanced to the next compartment.

The other important type of kiln is the tunnel kiln with the firing zone of oil burners in the middle of its length. Cold secondary air is preheated as it cools the fired bricks on their way out. Combustion gases preheat the advancing cold bricks. The heating cycle and time at top temperature are very important and vary from one type of brick to another. The firing temperature should be at least as high as that at which the brick is to be used to ensure completion of reactions and attain as high a degree of dimensional stability as is practicable.

Cooled bricks are ready for use. In a few cases storage properties are poor (dolomite). In some cases bricks are chemically bonded (e.g. with $MgSO_4$) and fired in the furnace after it has been built (e.g. chrome–magnesite). Special cases like these will be dealt with later.

Special refractories are made in the same general manner as has been described but the starting materials are very carefully purified "chemicals" rather than raw minerals. The size and grading are finer and more closely packed and the mixture must contain some kind of temporary bond which will be driven off during firing, leaving no harmful residue.

It seems likely that more extensive dressing of the minerals for ordinary refractories will be practised in the future so that closer control over composition will be achieved. This seems to be technically desirable for most basic refractories but the cost of such purification processes would be very high. These bricks are already very costly and any further increase in price would have to be adequately matched by improved performance in service.

13. Alumino-Silicate Refractories

The Alumina-silica System

The Al_2O_3–SiO_2 equilibrium diagram is shown in Fig. 9, with the composition of the various refractories marked on it. Up to 1545°C firebrick consists of mullite and silica. Mullite is present as needle-shaped crystals which form an interlocking matrix which can retain its strength and rigidity to high temperatures toward 1810°C at which it melts incongruently. The strength depends, of course, on the proportion of mullite present, i.e. on the Al_2O_3 content. Silica is present as tridymite or cristobalite (or both) (see page 120), but the effect of fluxes is to transform some of it to glassy silicates—thermodynamically very viscous liquids.

Above 1545°C liquid forms—again a very viscous liquid but viscosity falls off rapidly with temperature—and the structure becomes a matrix of mullite needles with liquid in the interstices. Considering siliceous firebrick (25 per cent Al_2O_3) we find that the proportion of liquid is about 70 per cent and it is unlikely that the remaining 30 per cent in the form of mullite will be able to maintain the shape of the brick for very long. The refractoriness of the brick has been exceeded at 1545°C and indeed probably at a lower temperature in the presence of fluxes. A brick containing 45 per cent Al_2O_3 on the other hand contains only 40 per cent liquid at 1545°C, the remaining 60 per cent being mullite, which remains solid. Temperature increases beyond 1545°C cause the amount of liquid to rise in all cases, but this rise is slow. At 1700°C the high-alumina brick has still only 45 per cent of liquid (although the other has 80 per cent and has undoubtedly slumped). It is clear that refractoriness in advance of 1700°C is quite possible with firebrick of suitable quality but R.U.L. values better than 1545°C will be difficult to attain.

Considering even higher Al_2O_3 content, at 72 per cent, at the mullite composition, the proportion of liquid at 1545°C has fallen

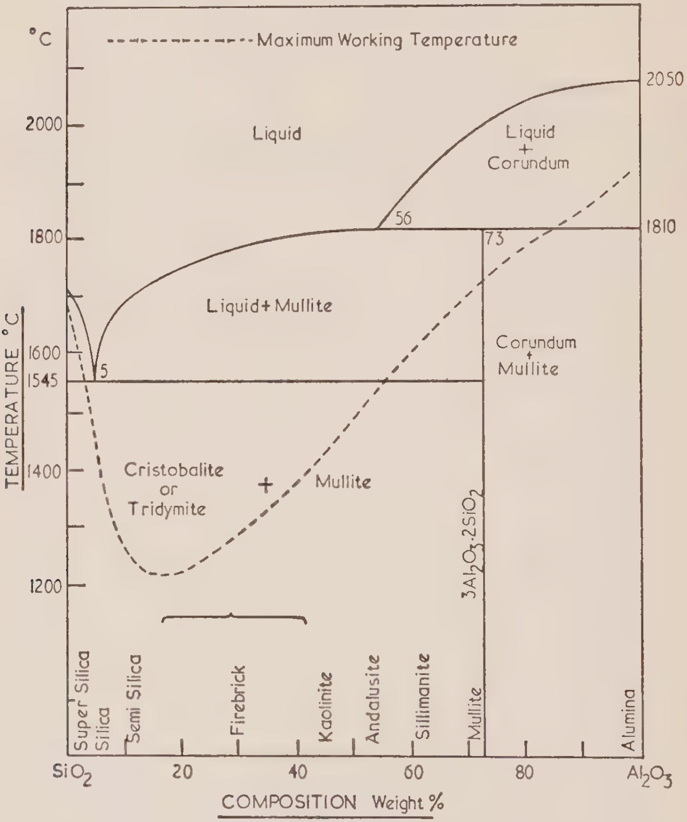

Fig. 9. The Al_2O_3–SiO_2 equilibrium diagram (after Bowen and Greig) indicating the compositions of various kinds of brick based on the system, and their approximate maximum working temperatures which depend also on other aspects of composition.

practically to zero and remains negligible up to 1810°C. The advantages of very high alumina are obvious and the development of bricks with Al_2O_3 content beyond the firebrick range will be discussed at the end of this chapter.

Firebricks

Firebricks are the commonest class of refractory—the "common brick" of the furnace designer. They are made from fireclay which usually occurs in association with coal measures and is plentiful in Britain though quality varies considerably, the best deposits being in the central Scottish coalfields. China-clay deposits in Cornwall have also been used in recent years to make a similar type of brick with enhanced properties.

Origins and Properties of Fireclays

Clays are produced by the decomposition of igneous rocks by geological agencies and conditions not commonly encountered today. The kind of clay depends on the kind of parent rock and presumably on the treatment it has had. Fireclay is derived from acid rocks like granite, in which felspars of the type $K_2O.Al_2O_3.6SiO_2$ are decomposed by H_2O and CO_2 (possibly at high pressure and temperature) to give K_2CO_3, SiO_2nH_2O, and $Al_2O_3.2SiO_2.2H_2O$. This last is the formula for kaolinite and also describes dickite and nacrite which have slightly different crystal forms, having been produced under different physical conditions. The structures of these clays are similar in that each is made up of alternate layers of "silica" and "gibbsite" ($Al(OH)_3$). The latter has itself a layered structure, a sheet of aluminium ions (Al^{3+}) being sandwiched between similar layers of hydroxyl ions (OH^-), each Al^{3+} ion being associated with 6 (OH^-) ions, each of which has a share in two Al^{3+} ions. The silica layers are also made up of three sheets of ions. The middle sheet is of hexagonally arranged Si^{4+} ions with O^{2-} ions tetrahedrally arranged round them so that on one side there are three O^{2-} ions, each sharing two Si^{4-} ions, and on the other side one

O^{2-} ion per Si^{4+} ion, this one unshared. The net effect is that there are too many O^{2-} ions for electrical stability and the silica sheet achieves its stability by incorporating its unshared O^{2-} ions into the gibbsite layer where they replace some of the $(OH)^-$ ions. There are several geometric arrangements whereby this can be achieved and these give rise to the slightly different minerals named and to halloysite which has rather more water incorporated in its structure. There are other groups of clay with different chemical composition, particularly the Montmorillonite–Beidelite group which also occurs in fireclay. These have formulae as follows:

Montmorillonite	$Al_2O_3.5SiO_2\ nH_2O\ (CaMg)\ O.$
Beidelite	$Al_2O_3\ 3SiO_2\ 4H_2O.$

The structure of these minerals is again layered "silica" and "gibbsite" but the order is different, there being more silica to accommodate so that there are two silica layers for every gibbsite layer. Further, aluminium ions may be partly replaced by magnesium ions which leaves an excess negative charge to be balanced by sodium, calcium and other cations which become loosely incorporated in the structure. These differences make this group of clays more plastic than the kaolinite group and their presence in fireclays renders them more workable than, say, china clay, but their lower alumina content and higher proportions of alkalies and alkaline earths impair refractoriness.

The clay material may have been purified and concentrated by the leaching out of soluble matter. The resultant "residual" deposit contains silica, micas, and clay, and is low in iron, alkalies and alkaline earths. The granular silica can be separated by elutriation as in the china-clay pits and the clay obtained is highly refractory, fires white and is mainly used for china. Otherwise the decomposed rock may have been washed away and separation of its constituents effected by differential settling in rivers or lakes. Such "transported" clay deposits are free of granular silica but may be contaminated by other substances, picked up during transportation, which impair refractoriness. The montmorillonite clays particularly can incorporate basic ions into their structure. Iron is a very common contaminant whose soluble salts are rather easily hydrolysed, depositing ferric hydroxide, often in small nodules.

Apart from essential clay substances many accessory minerals may be present in great or small amounts. These include free SiO_2 and Al_2O_3 from further weathering, iron oxide, carbonate, sulphide, titanate, and sulphate and salts of alkalies and alkaline earths, free TiO_2 and carbonaceous matter up to 15 per cent. These affect plasticity, refractoriness, and burning colour, and determine the usefulness of a deposit.

The very pure, white-firing china clay has been mentioned. The least pure clays derived from more basic rocks or heavily contaminated are red-firing and go to building bricks and drain-pipes. Intermediate grades are the very plastic ball clay, bond clay, flint fireclay, ordinary fireclay and aluminous fireclay, all with commercial uses.

Plasticity in clay corresponds to fluidity in a liquid. In liquids, flow occurs under all positive stress, velocity V being proportional to applied force P. Hence $V = K\phi P$ where ϕ is fluidity (Fig. 10a). In clays $V = K\mu (P - f)$ where μ is mobility and f is a yield stress below which there is no flow (Fig. 10b).

Both μ and f depend on the water/clay ratio of the mix (10c), but different clays behave quite differently (10d). Plasticity also depends on pH (10f) and grog additions increase the effective water/clay ratio and act like additions of water (10e) (grog being reckoned as clay when calculating the ratio). Plasticity was of particular importance in hand moulding and it is desirable to attain good plasticity without excessive water additions which are not easy to dry out. Even in machine moulding good plasticity is desirable in giving more uniform texture throughout the brick.

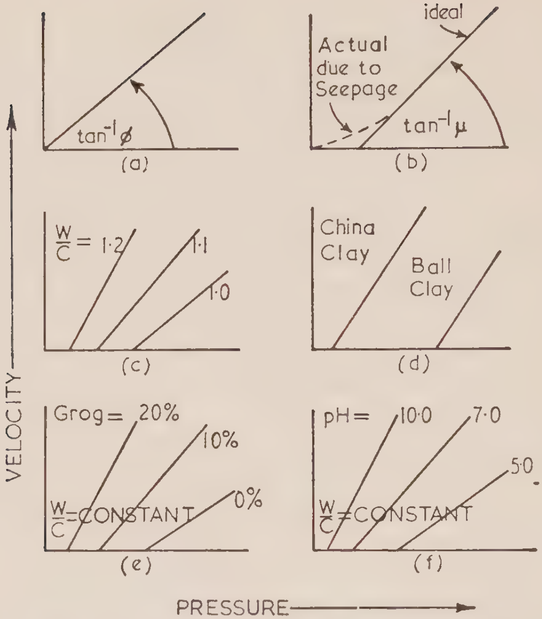

FIG. 10. Plasticity in clays. (a) Liquid; ϕ is fluidity. (b) Clay: μ is mobility: f is yield value of pressure. (c) Water: clay ratio (W/C) varies. (d) Clay type varies. (e) Proportion of grog varies. (f) pH varies.

Manufacture of Firebricks

The manufacture of firebricks follows closely the general description of the last chapter. Drying must be slow enough to avoid cracking, especially of hand-made bricks. Dry-press bricks are easily dried.

Firing follows three stages, as follows:

1. Smoking or Steaming—12–48 hr, from 20–300°C under reducing conditions. Mechanically and colloidally held water is expelled.

2. Decomposition—10–24 hr, up to 900°C in an oxidizing flame. Clays decompose over 500°C, combined water being

driven off leaving an amorphous residue sometimes called "metakaolinite". Any free α-quartz is converted to β-quartz above 573°C. Carbon and sulphur must be burned out because vitrification in stage 3 will prevent their later escape and leave the brick black-hearted.

3. Full firing—12–18 hr, up to 1200–1400°C. The formation of silicates probably proceeds from 1000°C onwards, and the upper permissible temperature depends on the progress of this vitrification. Silica and alumina are converted to higher temperature modifications and combine to form mullite at temperatures above about 1100°C. The top temperature depends on the proportion of fluxes present. Under-firing leaves the centre friable and weak. Over-firing may induce slumping and certainly causes high susceptibility to thermal shock.

The whole operation takes 3–5 days including cooling and the final structure will be mullite needles in a matrix of glass with any free silica as unchanged quartz or as tridymite or cristobalite.

Properties and Uses of Firebricks

Firebricks are classified by alumina content. Strict definition is by B.S.S. 1902 : 1952. Aluminous firebricks contain 38–45 per cent Al_2O_3. (Pure china clay contains 46 per cent Al_2O_3.) Ordinary firebricks contain up to 38 per cent Al_2O_3, the lower limit being defined by the proviso that SiO_2 must be less than 78 per cent—i.e. Al_2O_3 above about 22 per cent. Nevertheless, bricks with less than 32 per cent Al_2O_3 are of low quality and may be referred to loosely as siliceous firebricks. If Al_2O_3 is very low, between 10 and 22 per cent, the brick is called semi-silica and will be discussed later.

The levels at which other oxides may be found are shown in Table 7. Titania can be surprisingly high. Fe_2O_3 may come up to 3 or 4 per cent very readily. Alkalies may rise to 2 per cent but should be less than 0·5 per cent if possible. CaO and MgO usually account for another 1 or 2 per cent between them. It is the cumulative effect of these that is important in forming silicate bond in the firing stage and ultimately in fluxing the brick. They also act with slag in any attack on the brick. Obviously the lower these oxides are the better the brick is likely to be.

TABLE 7

Composition of Silica and Alumino-silicate Bricks

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O
High-duty silica	96/97	0·5/1·0	0·2	1·0	1·5	0·1	0·2
Silica	94/95	1·0/2·0	0·5	1·5	2·0	0·2	0·3
Semi-silica	88/90	8/9	0·5	1·0	0·2	0·2	0·4
Siliceous firebrick	63/65	26/28	Range 0·5 to 5·0, 1·5 typical	Range 0·7 to 6·0, 2·0 typical	Range 0·1 to 1·0, 0·5 typical	Range 0·3 to 2·0, 0·8 typical	Range 0·1 to 3·0, 1·5 typical
Firebrick	60/62	30/32					
Aluminous firebrick	50/52	40/42					
Andalusite	36/38	54/56					
Sillimanite	30/32	60/62					
Mullite	20/22	70/73					

Other typical properties of firebricks are listed in Table 8.

It will be seen that the refractoriness rises from about 1550°C to 1750°C as alumina rises from 25 to 45 per cent. Under load, however, softening is always evident at about 1500°C and may be even earlier depending on details of composition. Spalling resistance is usually good, the better again if alumina is high. Reversible thermal expansion (Fig. 6) compares favourably with other bricks.

Resistance to acid slags is generally good and resistance to FeO, basic slags and alkalies poor. Slag resistance depends to some extent on texture and is usually better in the higher alumina grades partly because of the alumina and partly because the proportion of alkalies and other fluxes is often rather lower in these more expensive bricks. The particular case of attack on alumino-silicates by iron blast-furnace type slags has been

TABLE 8

Typical Properties of Silica and Alumino-silicate Bricks

	Real density g/ml	Bulk density g/ml	Apparent porosity %	Refractoriness °C	R.U.L.	Spalling resistance	Slag resistance	Cold crushing strength lb/in.^{2}
High-duty silica	2·3	1·8	20	1730	50 lb/in.^{2} at 1600° No deformation		Good to acids	5000
Silica	2·3	1·7	25	1710	25 lb/in.^{2} at 1600° May fail within 1 hr	Good above 300°C	Fair to FeO	5000
Semi-silica	2·5	1·7	28	1450	Poor	Good	Good	2000
Siliceous firebrick	2·7	1·8	30	1550	1200/1300/1400°	Poor	Poor to bases	2000
Firebrick	2·6	1·9	26	1700	1450/1500/1550°	Fair	Poor to bases	3000
Aluminous firebrick	2·6	2·0	24	1750	1500/1550/1620°	Good	Fair	5000
Andalusite	2·8	2·4	22	1780	1520/1570/1640°	Good	Fair	4000
Sillimanite	3·0	2·3	22	1810	1550/1600/1650°	Good	Good	6000
Mullite	3·2	2·2	22	1850	1570/1610/1690°	Good	Good to FeO	9000
Insulating firebrick	2·7	0·95	66	1700	Poor	Poor	Poor	500

thoroughly investigated by Ford and White[1] using the CaO–SiO_2–Al_2O_3 ternary diagram, a liquidus surface of which is reproduced in Fig. 11. This diagram is probably quite accurate and has great technological significance for ceramists and metallurgists. Compositions corresponding to about 20 per cent of slag and 80 per cent of firebrick all lie in the field in which the primary phase is mullite and the slope of the liquidus surface down to the eutectic trough between the mullite and anorthite fields is so steep that at say 20 per cent slag and 1500°C, even ignoring the contribution of fluxes from the brick itself, about 90 per cent liquid can be expected. Even at the sillimanite composition where corundum separates first, things are no better and the eutectic valley between mullite and anorthite dominates the whole range of possibilities below the mullite composition. Detailed examination of vertical sections indicates that the optimum Al_2O_3 content is about 44 per cent, i.e. opposite the point 1512° on the diagram, at the top end of the mullite–anorthite eutectic valley, where the slope of the liquidus is least and the proportion of liquid formed with, say, 20 per cent of slag at 1500°C is also least (nil on the diagram up to 1512°). Beyond 70 per cent Al_2O_3 it is obvious even from Fig. 11 that 20 per cent of blast-furnace slag could be absorbed without formation of much liquid at 1500°C but mullite bricks are, of course, very much more expensive than firebricks and are not made from indigenous rock.

The effect of FeO on these bricks is important but the FeO–AlO_3–SiO_2 diagram is incomplete. Towers,[2] however, has discussed the attack of alkalies on firebricks and shows that high-alumina firebrick resists the attack much better than siliceous firebrick by considering the Na_2O–SiO_2–AlO_3 diagram. The inherently viscous nature of molten silicates must play an important part in delaying the failure of these bricks under corrosive conditions. Provided the glassy products of the initial attack do not flow off the surface they provide protection against further direct attack and render indirect attack by diffusion a very slow process. This is probably more effective in the siliceous firebricks than in the high-alumina ones.

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[1] W. F. Ford and J. White, *Trans. Brit. Ceram. Soc.* 50, 1951, p. 461.

[2] H. Towers, *Iron and Steel*, 28, 1955, p. 101.

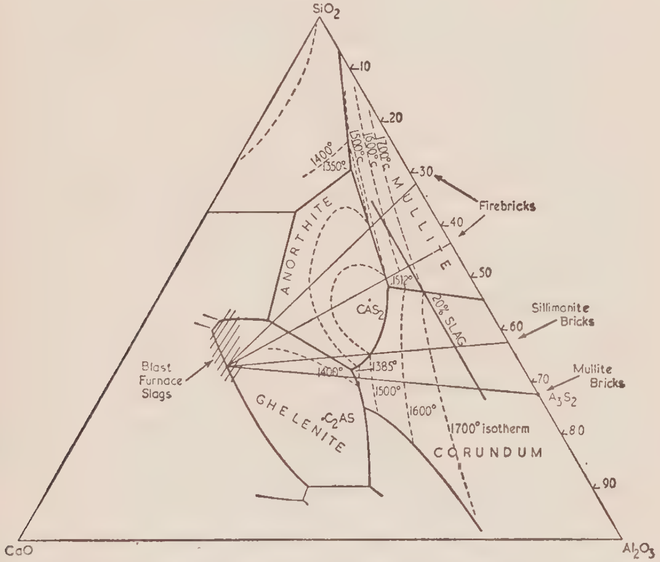

FIG. 11. Part of the liquidus surface of the $CaO–SiO_2–Al_2O_3$ equilibrium diagram (after Greig, Rankin and Wright) drawn to show the relationship between blast-furnace slag compositions and those of various alumino–silicate bricks.

Firebricks are sometimes subject to carbon deposition from CO in furnace atmospheres at temperatures about 450°C ($2CO = CO_2 + C$). This is catalysed by "iron-spots" which should be absent. These are derived from particles of iron oxide or sulphide in the clay. Hard-firing converts all iron to silicate, when it is harmless, but must not, of course, slag the brick in the process. Low porosity and particularly low permeability restrict access to this gas. A special test may be necessary to ensure a brick to be proof against this form of failure, particularly when the brick is to be used in the stack of a blast furnace. A sample is held in a stream of carbon monoxide at 450°C for up to 200 hr and examined at intervals for signs of carbon deposition, cracking or disintegration (see B.S.S. 1902 : 1952).

Hard firing is also a means of increasing abrasion resistance. This is by partial vitrification and consequent reduction of porosity, resulting in a more compact and harder brick. Spalling resistance may suffer. In such a brick high refractoriness need not always be necessary.

Incorporation of grog—prefired clay or crushed broken brick—in the clay mix usually leads to a harder brick with good spalling resistance as advancing cracks must find their way around grog particles. Grog is advantageous in a number of respects in the manufacturing stages too.

Firebricks are the common brick of the furnace designer. They appear in various qualities all over industry where heat is applied as well as in the domestic fireplaces and stoves. They are moderately cheap and the material is indigenous and traditional. Replacement at special points has been steadily going on for forty years but they still dominate the scene.

In ironworks they appear in blast-furnace stack, bosch and hearth and in ladles. They fill the Cowper stoves and line the hot-blast main and blast-furnace main. In steelworks they appear in the open hearth but not exposed to the steelmaking temperatures. They fill the checkers, line the ladle, form its stopper, and appear in the casting bay as runners and guide tubes. Again in the soaking pit and reheating furnace firebrick is the basic building material. It appears too in small furnaces in foundries and in non-ferrous industries and in all types of steam-raising plant. The quality used depends on the conditions prevailing and obviously the cheapest that will do the job should be employed. High alumina qualities go into the blast furnace and many of the steel plant applications, e.g. at the *top* of the Cowper stove and checker assemblies where high temperatures or potentially slagging conditions are met. The blast-furnace stack is liable to carbon deposition and here china-clay bricks (no iron), made to very low porosity for high abrasion resistance, have been tried. In ladles a quality which can be relied upon to "bloat" or expand on heating, that is having by design a high after expansion, is used to ensure tight jointing (see Fig. 6). This bloating seems to be due to an evolution of gas (probably SO_2) after the porosity has been sealed off and when the brick has started to soften.

High Alumina Bricks

It is obvious that increases in Al_2O_3 content beyond 46 per cent would be beneficial, but there are no suitable clays in Britain to make such bricks so that minerals have to be imported for the purpose. Sillimanite ($Al_2O_3.SiO_2$), imported from Assam, containing 63 per cent Al_2O_3 was first used in the 1930's, but is today replaced by Kyanite from Africa. Recently South African Andalusite (of the same composition as Sillimanite and Kyanite but a different crystal habit) has been adopted to make a brick of 50 per cent Al_2O_3. These minerals are in the form of rocks and may be used as mined, or blended with clays to obtain intermediate compositions. The terms Sillimanite and Andalusite are applied to the bricks although the constitution after firing is mullite, glass and cristobalite or tridymite as in the firebrick, except that the proportion of mullite is higher and the amount of fluxes probably lower.

Bricks are made also to 70–73 per cent Al_2O_3, called Mullite bricks, and containing very little free silica after firing. Bauxite must be used to raise the alumina content this far. Alumina bricks are made entirely from bauxite with a small amount of clay added as a bond. The bauxite may be pre-fused, crushed and ground, but this makes a very expensive brick. Such a brick is entirely mullite and corundum and remains solid up to 1810°C (Fig. 9). These products are progressively more expensive than firebricks and their use is limited to places where conditions are severe. Table 8 shows how refractoriness improves at least up to the mullite composition, and there is a steady improvement in hot strength through the range, while spalling resistance remains excellent. The cold crushing strength of some of these bricks is extremely high and they are used where liable to heavy mechanical wear or abrasion, and not necessarily always at very high temperatures. Resistance to slagging is generally rather better than that of firebricks. The 50–60 per cent Al_2O_3 bricks stand up to acid slags and glasses, but at 70 per cent Al_2O_3 resistance even to FeO and lime is quite good. None remain unaffected by alkalies but high Al_2O_3 is an advantage here too and these bricks are used in glass tanks.

The 50–60 per cent bricks are used in open-hearth checkers and Cowper stove combustion chambers and domes, in soaking pits and reheating furnace walls and roofs, in ladles, and on furnace doors—replacing aluminous firebrick in many cases.

The mullite type might be found in electric furnace crowns, in the hearths of reheating furnaces and lower parts of soaking pits where FeO attack is severe. Non-ferrous applications include brass melting reverberatories, lead drossing reverberatories and aluminium melting furnaces. There are non-metallurgical uses too in glass, cement, pottery and enamelling industries. The alumina (95 per cent) brick has still few applications to justify its cost.

Each type of these bricks can be prepared to a range of specifications, the control being mainly through manipulation of the porosity. The properties listed in Table 8 are only typical and no attempt is made to indicate the ranges within which the individual values may lie.

14. Silica Bricks

RATHER pure silica is required for brick-making—not less than 95 per cent SiO_2 and with less than 1 per cent Al_2O_3 and 0·3 per cent alkalies. Ganister, quartzite, sand and flint are all used, and from South Africa micro-crystalline material called silcrete which has TiO_2 as a major impurity. Other sources of suitable material are continuously being sought.

Ganister is clay-bonded sandstone and has been used raw in furnace construction for centuries. In the South Pennines there are ganisters with up to 98 per cent SiO_2 suitable for brick-making. Most ganisters are expensive to mine and quartzite, mainly from Wales, has been the chief source of silica in Britain in recent years, although these reserves are running low. This is a sandstone bonded with colloidal silica and is very hard. Sand may be blended with quartzite, and broken bricks are returned like grog.

The quality of the brick depends on the crystal size of the rock, so that not all quartzites are suitable. Certain types with very fine crystals and silcrete which shows a conchoidal fracture and extremely fine structure, fire to a brick of unusually low porosity, and, other things being equal, enhanced properties. There has been developed in recent years a grade called high-duty silica bricks derived from specially selected materials, high in SiO_2, low in Al_2O_3 and alkalies, and of very fine grain size and low porosity.

Allotropy in Silica

There are said to be 15 modifications of silica. The important forms are set out in Fig. 12 to show their ranges of stability and the volume changes occurring on transformation, according to Sosman.[1]

The naturally occurring form is α-quartz, which transforms rapidly and reversibly to β-quartz at 573°C. The volume change is 1·35 per cent, large enough to shatter a piece of the material or an unfired brick unless heating past this temperature is very slow. β-quartz is stable to 867°C but may persist to much higher temperatures. Its conversion to tridymite is slow unless catalysed by a mineralizer such as calcium tungstate, as a considerable degree of atomic reorganization must occur. Mineralizers are usually fluxes and cannot be used in sufficient quantity to effect rapid transformation in bricks. However, cracking is not likely during slow transformation. Above 1470°C cristobalite is the stable form and again the transformations, either from tridymite or from quartz, are slow. Cristobalite remains stable to the melting point at 1723°C.

Sosman's classification shows conversion of quartz and tridymite to glass rather than cristobalite at 1450°C and 1680°C respectively. Liquid, on cooling, forms glass or vitreous silica, which is of course a metastable form, and devitrification to cristobalite could occur in time if a high temperature were maintained and particularly in the presence of a suitable mineralizer.

Cristobalite, when cooled below 1470°C, can revert to tridymite, but this is slow and usually it persists as metastable cristobalite to room temperature but with a complex transformation at 275–200°C to a low temperature variety. Similarly, tridymite persists to low temperatures with modifications at 475°, 210°, 163° and 117°C.

The volume changes involved are rather high for such a low temperature and rather spectacular shattering occurs unless the temperature is lowered very slowly from 300° to 100°C. Similarly, on reheating, great care must be taken to avoid spalling and to accommodate the expansion in the furnace.

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[1] R. B. Sosman, *The Properties of Silica* (American Chemical Society Monograph, 1927).

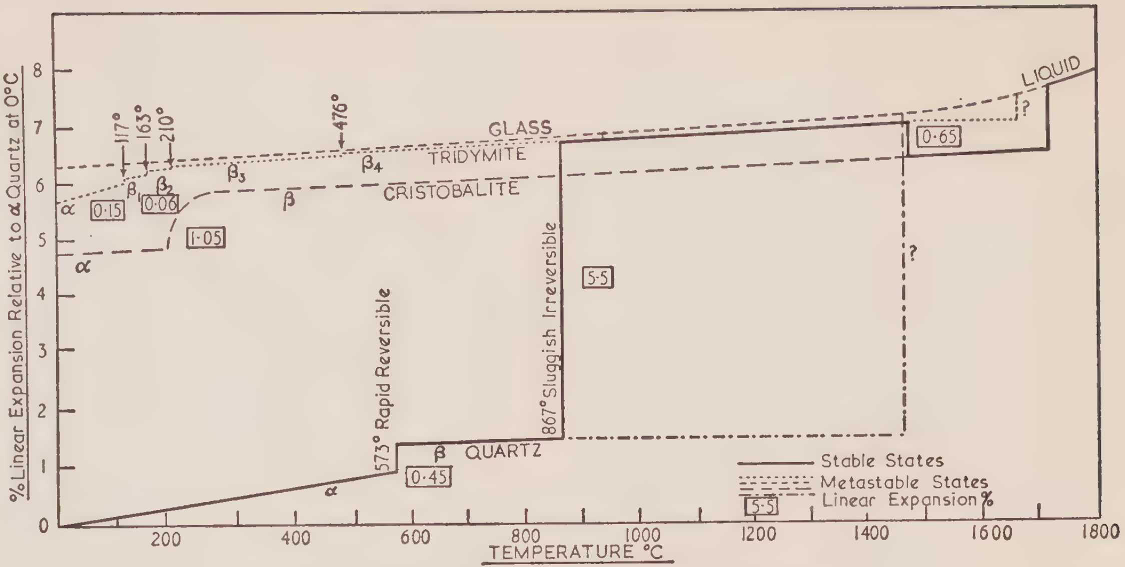

FIG. 12. Allotropy in silica and the associated volume changes.

Note: The line for glass probably ought to dip below the tridymite line in the middle range of temperature but has been drawn above it at all points for clarity.

In a few respects observed phenomena are not consistent with Sosman's classification (or Fig. 12). Devitrification of glass is always to cristobalite even at temperatures below 1470°C where crystobalite is, on the diagram, metastable. Similarly crystobalite is found in firebricks rather than tridymite even after firing below 1470°C. The phase formed would appear to be strongly dependent on the particular fluxes or mineralizers present. In Fig. 12 the glass is shown for convenience as being less dense than tridymite at all temperatures. In fact the super-cooled liquid is usually shown as rather more dense than tridymite. It is rather unusual to find a solid less dense than the corresponding liquid and this is further support for the view that the classification is not really satisfactory and that tridymite is only stable in the presence of some impurities. The classification does, however, satisfactorily describe the behaviour of most commercial forms of silica, with the exceptions noted.

Manufacture

Manufacture follows the usual pattern. Crushing should aim at production of angular particles. Grading is important. Lime water is added to about 1·7 per cent CaO to form a temporary bond and also gives some plasticity. Moulding is by dry-press method. Firing may take up to two weeks and should attain about 1500°C. It is a very long process because it involves a number of changes of crystal form, some of which are very slow, some rapid and liable to disrupt the brick (see Fig. 12). Heating past 573°C must be slow to accommodate quartz and cooling between 300°C and 100°C must also be very slow to avoid cracking as the high temperature forms of tridymite and cristobalite transform to the room temperature modifications. The time of soaking at the top temperature depends on which modification—tridymite or cristobalite—is desired to be predominant.

It is usual to fire "hard" so that no quartz is left in a brick. Then after-expansion is low, and all the care has to be taken up to 300°C only, on heating up the furnace. No trouble at 600°C need be anticipated. (Soft firing is adopted in Germany apparently because they prefer a less sudden expansion over a longer period.) The resulting brick is then a mixture of tridymite and cristobalite depending on the firing temperature and time, and the prevalence of suitable mineralizers. Where occasional cooling toward 200°C may occur the brick should be mainly tridymite. During high temperature work, however, gradual conversion to cristobalite is likely, and most bricks will be made with much of that form present when new. The constitution is reflected in the density of a brick, compared with the densities of quartz 2·65, tridymite 2·26, and cristobalite 2·32 g/ml.

Bonding of the particles in the bricks is partly by formation of calcium silicate glass and partly through an interlocking action between tridymite needles. The most valuable property of silica bricks is a very high R.U.L. which is due to this tridymite bond. Rigidity can be maintained even under load very close to the melting point. It might seem that 1·7 per cent CaO is rather a powerful flux in such a brick. Fig. 13 shows, however, that there is a "monotectic" reaction at 1690°C in the $CaO–SiO_2$ system below which only a very small proportion of liquid can form—about 5 per cent with 1·7 per cent CaO, down to 1440°C. This has little weakening effect on the strong tridymite skeleton. FeO, MgO and MnO behave in a similar manner (Figs. 8 and 14) with silica but Al_2O_3 and TiO_2 both form eutectics with SiO_2 at about 1545°C with 6 per cent and 10 per cent additions respectively (see Fig. 9). These and alkalies should be kept low in general but TiO_2 itself can be tolerated in some of the high-duty bricks of the silcrete type.

Properties and Uses

Refractoriness of silica bricks is often quoted up to 1710°C—formerly adopted as the melting point. Occasionally even higher values are obtained for new high-duty bricks—e.g. 1730°C.

Under load, initial softening occurs at about 1630°C in ordinary qualities and up to 1670°–1700°C in high-duty bricks. In maintained temperature tests, however, 10 per cent subsidence would occur at 1450°C in an hour in ordinary grades and at 1650°C in 2 hr in the higher quality. The improvement in developing the high-duty bricks is considerable, although the cost is high. The thermal expansion of silica between the allotropic change points is very low, and spalling resistance above 300°C is therefore very good, although so poor below that temperature

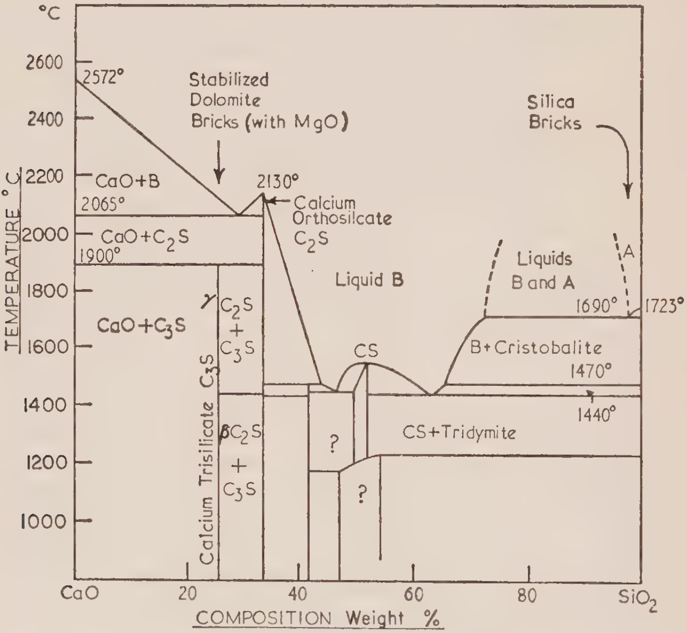

Fig. 13. The $CaO–SiO_2$ equilibrium diagram (after Rankin and Wright: and Greig) showing the "monotectic" point and wide immiscibility gap which control the liquid content at a low level even in the presence of some CaO. The trisilicate and orthosilicate of calcium used in the stabilization of dolomite also appear in this diagram.

Note the notation: C = CaO, S = SiO_2, C_3S = $3CaO.SiO_2$. In other diagrams F = FeO, A = Al_2O_3, M = MgO.

(see Fig. 12). Resistance to slagging is remarkably good, considering the extremely acid nature of the brick. Permeability is usually very low indeed and porosity is held as low as possible, i.e. down to about 15 per cent in the high-duty bricks. It is again the form of the CaO–SiO$_2$, FeO–SiO$_2$ and MnO–SiO$_2$ equilibrium diagrams which is mainly responsible, however, for the resistance to slagging, coupled with the very high viscosity of the product of reaction. Not only acid slags, but FeO and to a lesser extent basic slags have much less effect than one would expect from a consideration of the simple chemistry of the case.

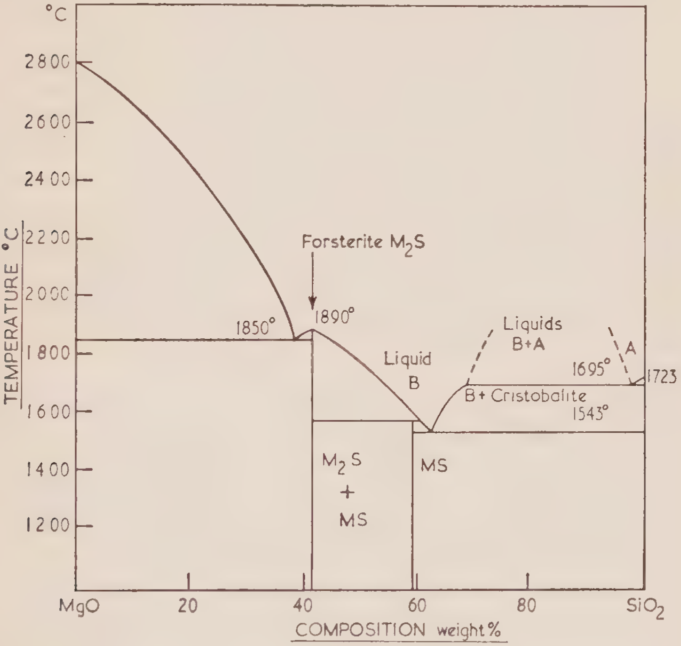

Fig. 14. The MgO–SiO$_2$ equilibrium diagram (after Bowen and Anderson) showing the "monotectic" point on the right-hand side, and also the very refractory nature of forsterite M$_2$S compared with MS.

Silica brick, with a bulk density about 1·8, is a fairly light brick—an advantage in some of its applications over alternatives. Silica bricks have two major applications. In the roof of reverberatory furnaces, and particularly the open-hearth steel-making furnace, silica was for long the only material capable of withstanding the compressive forces in an arched roof at temperatures up to 1600°C. Its lightness reduced these forces to a minimum. Its low expansion favoured stability in the large structure. Its high R.U.L. permitted it to carry the great load up to high temperatures—much of the load being taken by the "cold" end however. Its high refractoriness minimizes drip from the hot face, and that face is not unduly attacked by slag splash from the bath. Nevertheless, it is in these roofs that high-duty silica bricks are now being used either in patches in vulnerable areas or as a "zebra" roof, alternate rows of brick being high-duty and projecting forward to screen the cheaper bricks between from the worst of the heat.

Normal failure of such brickwork is by gradual solution of the hot face by fluxes thrown up from the bath below. Molten silicates drip back into the bath. At the same time, changes occur in the bricks which develop a banded appearance in sections. There is a dense grey cristobalite zone at the hot face, ahead of the 1470°C isotherm, backed by a darker zone of tridymite. Then there is a narrow zone into which fluxes, including Al_2O_3, have migrated back from the hotter zones. Behind this there is an unchanged zone. The loss of fluxes from the cristobalite zone may cause its refractoriness to be higher than that of the original brick in spite of absorption of FeO from the process, but there a tendency develops toward structural spalling through the interfaces between the zones and particularly where the fluxes have segregated. If this zone is exposed by such spalling, lateral attack by slag can be severe.

Other reasons for failure are damage by thermal spalling during heating up, which should not exceed the rate of about 10° per hour between 200° and 300°C, and overheating by, for example, direct flame impingement which causes rapid slagging off and even straight melting of the brick, until the roof is dangerously thin.

The second major application is as the oven walls of coke-ovens. Here a thin wall (for rapid heat transfer) is required to stand at 1400°C almost indefinitely. Silica bricks of high quality were originally developed for this purpose.

The acid open-hearth furnace is built largely of silica and the hearth is lined with ganister. Some electric furnaces are also mainly in silica, and Bessemer converters are usually lined with soft-fired silica brick and have firebrick tuyeres. Silica also appears in such places as Cowper stove domes and top runs in checkers though high alumina bricks are now used in these places too.

A furnace with silica brickwork is almost impossible to cool below 300°C. This is a major restriction on the use of this refractory.

Semi-silica Bricks are prepared from low-grade ganisters or from artificial sand/clay mixtures. Their properties lie between those of silica and firebricks. They are cheap and have the advantage over firebricks of low after-shrinkage and over silica of better spalling resistance. Slag attack usually looks very severe but is actually restricted to a glazing of the surface. It has been suggested that this brick is always far from equilibrium, remaining always a firebrick matrix with silica particles embedded in it. These bricks are used as cheap backing for silica in places where conditions are not severe or in places where silica would be the choice at a rather higher temperature level. Examples of uses are in coke-ovens, kiln roofs and flues.

15. Magnesite-Chromite Refractories

Magnesite

Lime and magnesia are among the most refractory oxides melting at 2570°C and 2800°C respectively. Unfortunately, lime cannot be dead-burned to become inert to water and its use, as a pure oxide, is restricted to platinum metallurgy.

Magnesia is neither so plentiful nor so cheap as lime. It has traditionally been prepared from magnesite ($MgCO_3$) or breunnerite which contains also some $FeCO_3$. The best deposits are in Austria and Czechoslovakia but Greece, Yugoslavia, India, Australia, South Africa and California all have useful supplies. Russia and Manchuria also produce magnesite. British deposits are poor and here we have turned to the sea as our main source of magnesium, and America also uses the sea for part of her requirements.

Magnesite is prepared if necessary to lower $CaCO_3$ and $FeCO_3$ content by "ore-dressing" techniques—grinding and washing or calcination and magnetic separation—and is then fired in rotary kilns over 900°C to form the oxide and then beyond 1600°C to produce the compact form of magnesia called periclase, which is stable to water. This is known as "dead-burned magnesite".

Sea water contains 0·2 per cent MgO (as $MgCl_2$) so that 110,000 gal or about 500 tons have to be treated to obtain 1 ton of MgO. The chemistry involved is simple. Dolomite is calcined to a mixture of CaO and MgO, called doloma, which is added to the sea water. The oxides hydrate, and $Ca(OH)_2$ reacts with $MgCl_2$, giving $Mg(OH)_2$ which precipitates while Ca goes into solution as chloride. A number of side processes have to be operated to reduce contamination of the magnesite by impurities in the burned dolomite, and by calcium as the carbonate or sulphate in the sea water itself. Precipitation should be controlled to give very complete yield of MgO and to produce large crystals which will settle out rapidly in the thickeners. After being separated by filtration, the hydroxide must be dead-burned to periclase as described above.

Brick manufacture is quite straightforward. The clinker is crushed and sized and the grades blended with bonds such as milk of magnesia, hydrated ferric oxide or clay and not over 5 per cent water. Moulding is by dry press at 15,000 $lb/in.^2$ This high pressure is necessary to give good green strength and fired strength; to minimize shrinkage in firing; and to reduce porosity and improve R.U.L.

The bond which develops is a cement of small crystals of silicates and other compounds. Silica is an inevitable impurity and the desirable compound is forsterite, $2MgO.SiO_2$, which melts at 1900°C. Additions of pure MgO in the finest grades are made to increase the $MgO–SiO_2$ ratio in the bond and hence improve the refractoriness (see Fig. 14). Silicates of iron and calcium and even magnesium ferrite may also form.

In basic bricks refractoriness and strength depend on the properties of this cement, and ultimately on its melting point. The corresponding liquids are not usually viscous. There is no interlocking of acicular crystals, as most of the cement constituents are of cubic habit.

Properties and Uses

Refractoriness of these bricks is about 1800°C, but R.U.L. is not above 1500°C. Spalling resistance is also poor, probably owing to the high coefficient of thermal expansion (see Fig. 6), but some grades now show 30 + reversals. Zirconia is sometimes blended in to this end. "Structural spalling" also occurs due to a swelling caused by absorption of FeO in certain circumstances. Flakes then break off the hot face. Resistance to slags rich in CaO and FeO is extremely good, and even acid slag attack is inhibited by the formation of the high melting forsterite ($2MgO.SiO_2$). Thermal conductivity is very high. Bricks are rather dense, light brown in colour and slightly magnetic.

Magnesite bricks are used in basic electric and open-hearth furnaces, under the hearth and in the walls to some extent. They have been used in roofs, too, and as linings for mixers. Their slag resistance also makes them a possible choice for the top runs of checker work, provided that bricks of high spalling resistance can be supplied.

Magnesite may be built into monolithic walls by metal casing with mild steel which oxidizes and cements adjacent bricks together. Tubing rammed with dead-burned magnesite and assembled into walls before heating up to 1400°C also consolidates into strong structures relatively free from spalling troubles. This type of wall has been used in the kilns in which the bricks are fired, and in electric arc furnaces.

Crushed magnesite can be used for making the working hearth. It is milled to $\frac{1}{4}$ in. for high packing density and rammed in with tar to a template and the tar burned out *in situ*. Similar pea-sized material without the fines can also be used for fettling between heats. In these applications in Britain, however, doloma is more likely to be the economic choice than magnesia.

Dolomite

There are vast deposits of dolomite in Britain. It usually contains an excess of CaO over that in the true double carbonate $MgCa(CO_3)_2$, useful material having about 30 per cent CaO and 20 per cent MgO with CO_2 and varying small amounts of SiO_2 (say 0·5 per cent), Al_2O_3 and Fe_2O_3. It can readily be calcined to mixed oxides ("doloma") but cannot be "dead"-burned. The CaO is always reactive to water. MgO and CaO form an eutectic at 32 per cent CaO and 2300°C. Before dolomite can be used as a brick the CaO must be stabilized or the brick will crumble in moist air. This is done by combining it with silica. There are two possible silicates—the trisilicate $3CaO.SiO_2$ and the orthosilicate $2CaO.SiO_2$ (see Fig. 13). The former dissociates at 1900°C to form CaO and the *o*-silicate which melts at 2130°C. The *o*-silicate has three modifications, γ above 1410°C, β between 1410°C and 678°C, and α below 678°C. The $\beta \rightarrow \alpha$ change involves a 10 per cent volume change which causes "dusting" (material falls to a powder) though this can be inhibited by additions of Cr_2O_3, B_2O_3 or P_2O_5 (which adversely affect slag resistance).

In U.S.A. stabilization is by formation of the orthosilicate (inhibited) but in Britain the trisilicate is favoured, with a small excess of SiO_2, to throw errors on the safer side.

Manufacture

Silica is added as serpentine ($3MgO.2SiO_2.H_2O$) before calcining and the mixture fired in a rotary kiln at about 1600°C to a stabilized clinker, containing periclase, the calcium silicates and aluminates, or ferrates of calcium and magnesium. The clinker is crushed and sized, graded and tempered with 4 per cent water, dry-press moulded at 10,000 $lb/in.^2$, dried and fired at 1400°C. If stabilization is not complete it shows at the drying stage. The finished brick should withstand 24 hr in boiling water without change. These are Stabilized Dolomite bricks. A cheaper product is the Semi-stabilized brick. Shrunk dolomite is mixed with Fe_2O_3 and Al_2O_3 as bonds and then with heavy oils as a temporary bond. The oil has to carry the Fe_2O_3 and Al_2O_3 all over the clinker surface and keep out moisture until the bricks are in the kiln. Firing is at 1400°C and bricks must be put into service at once, unless they are specially prepared for storage with a coating of a tarry material. Under favourable conditions storage up to a year is possible, but the CaO is always active toward moisture.

Properties and Uses

Analyses of the two types of dolomite brick are compared in Table 9 and properties in Table 10. The properties are not very good. Refractoriness is high as in all basic bricks, but under load it falls to 1450°–1550°C for stabilized and 1350°–1450°C for semi-stable bricks. Spalling resistance of the stable brick is often poor, but a spalling-resistant grade can be made; that of the semi-stable brick is moderately good (20 cycles). Slag resistance is poor, attack being mainly through the bond. Doping with fine MgO to make forsterite can improve this property. Semi-stable bricks are again rather better in this respect.

TABLE 9

Composition of Basic Bricks

	MgO	CaO	Cr_2O_3	SiO_2	Al_2O_3	Fe_2O_3	
Magnesite	85/90	1/3	—	2/3	1/3	2/5	Up to 0·2% MnO and 0·5% TiO_2 may occur in all types
Chromite	15/20	1/2	30/40	4/6	15/20	12/15	
Chrome-magnesite	38/40	1/2	28/30	4/6	15/20	10/15	
Magnesite-chrome	65/75	1/2	6/10	3/4	4/6	4/6	
Stabilized dolomite	40/42	38/40	—	12/15	2/3	2/3	
Semi-stable dolomite	36/40	48/50	—	3/5	2/3	2/3	
Forsterite	50/60	0·5/1·0	—	30/40	2/3	6/8	

The use of dolomite bricks is mainly in the basic open-hearth furnace, in the hearth and side and end walls and banks, but usually only as a part replacement for magnesite. Miscellaneous uses include ladle linings and stopper sleeves. Similar applications occur in electric arc, and tilting open-hearth furnaces. The main value of dolomite is its cheapness. Semi-stable bricks are used particularly where the brickworks is near the steel plant so that they can be built in and the furnace heated before crumbling starts.

Like magnesite, dolomite is used in crushed form, pea-size and tarred for ramming hearths, and for fettling.

TABLE 10

Typical Properties of Basic Bricks

	Real density g/ml	Bulk* density g/ml	Porosity %	Refractoriness °C†	R.U.L.		Spalling resistance	Cold crushing strength lb/in.^{2}
					Rising§ temperature °C	Maintained temperature		
Magnesite	3·5	2·8	19/24	Very high in all cases above 1750°C	1450–1500 1500–1650 1550–1720	Slow failure at 1600°C in all cases	Two kinds one poor‡ one good	10,000
Chromite	4·0	3·0	22/27		1250–1350 1350–1450 1400–1600	The best creep at 1400°C	Poor	7000
Chrome–magnesite	3·9	3·0	20/25		1350–1500 1450–1600 1600–1730	The best deform at 1600°C	Very good	4000
Magnesite–chrome	3·6	2·9	20/23					
Stabilized dolomite	3·3	2·5	22/24		1450–1550 1500–1600 1600–1650	—	Poor	8000
Semi-stable dolomite	3·3	2·5	22/24		1350 1500 1600	—	Good	5000
Forsterite	3·4	2·6	20/23		1550 1600 1650	Deformation at 1600°C is slow	Fair	4000

* Bulk density largely dependent on porosity.

† Values seldom quoted.

‡ Controlled by grading and porosity.

§ R.U.L. very variable—depends on bond.

Forsterite

This silicate of magnesium has been mentioned as having good refractory properties—see Fig. 14. It is one of the olivenes and occurs in dunite in which it is strongly contaminated with varying amounts of FeO replacing MgO. Olivenes decompose to minerals like serpentine ($3MgO.2SiO_2.2H_2O$) and talc and steatite (both $3MgO.4SiO.2H_2O$), and all of these are used to make forsterite bricks. Very fine magnesia is added to boost the MgO in the bond and the mixture is dry-pressed and fired.

Refractoriness depends upon the iron content, which should be as low as possible, and should be about 1750°C. Under load, the bricks are typical of basic bricks, deforming slowly at any temperature beyond 1550°C. Thermal expansion is low and spalling resistance only moderately good. The refractory is resistant to both acid and basic slags, though perhaps not so much as silica on the one hand and chrome magnesite on the other. Resistance to FeO is also good but it is not better than chrome magnesite. Uses of forsterite are rather specialized and limited. The most important is in copper smelting, but it has been applied to open-hearth back walls with moderate success, in downtakes, and top courses of checker-work. Both the brick and its applications may well still be in a state of development, and there could be a future for a refractory made of the pure compound.

Chromite

The spinels are a group of minerals with the general formula

$$R''O.R_2'''O_3$$

where $R'' = Fe^{++}, Mg^{++}, Mn^{++}$, etc. (but not Ca^{++}),
and $R''' = Fe^{+++}, Al^{+++}, Cr^{++}$, etc.

Hence	$MgO.Al_2O_3$	Spinel
	Fe_3O_4	Magnetite
	$FeO.Al_2O_3$	Hercynite
	$MgO.Cr_2O_3$	Picrochromite
and	$FeO.Cr_2O_3$	Chromite

are members of this group. These have all cubic crystal structure and are hard and refractory and all are mutually soluble. Only spinel itself has been used pure as a special refractory. It can be fused with B_2O_3 as mineralizer, and cast in moulds, and Chesters[9] mentions one application to the linings of induction melting furnaces which can be made impermeable to molten steel from MgO–Al_2O_3 mixtures which expand when they combine on heating to form spinel (cf. bloating firebricks for ladles). Chromite, however, gives its name to a type of brick made from chromite ore which is usually a mixture of chromite and picrochromite. Chromite ores are found in many countries—Greece, Turkey, Rhodesia, Cuba—and vary greatly in composition. Those with highest chromium content go to metal production. Of the remainder those with high MgO and low FeO are used for brick-making.

A typical Cuban ore has 31 per cent Cr_2O_3, 29 per cent Al_2O_3, 18 per cent MgO, 16 per cent FeO, 5 per cent SiO_2 and 0·4 per cent CaO. Obviously this is far removed from the composition of pure chromite.

Chromite bricks are made by standard methods. Bonds may be added—fine lime or hydrated magnesia or (temporarily) tar. Firing is at 1450°C usually on top of magnesite because their low green strength does not permit stacking these bricks in the kiln.

Properties and Uses

The refractoriness of chromite bricks is about 1700°–1850°C, depending on the ore used. Their R.U.L. is poor and they cannot be trusted beyond about 1400°C owing to the possibility of there being $MgO.SiO_2$ in the bond (see Fig. 14). Spalling resistance is very poor, thermal conductivity being about the same as that of magnesite. The colour is distinctively black and the density high at three. The only valuable property is an extremely high resistance to attack by either acid or basic slag.

Chromite brick is the "most neutral" refractory and its limited uses all exploit this unique feature. The most important application is as a single neutral course between the basic walls and acid roof of a basic open-hearth furnace. It also appears in the bottom of some soaking pits, protecting firebrick from FeO, and in acid open-hearth furnaces protecting SiO_2 at the ports. Other possible applications, e.g. at slag lines or in ladles, are limited by the poor general properties.

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[9] *see* bibliography.

Chrome Magnesite and Magnesite Chrome

The natural development of the chromite brick (which is not chromite at all, but depends on its MgO content) was the modification of the MgO proportion and condition. Refractoriness is enhanced by increasing the MgO–SiO_2 ratio, especially in the bond. This is done by adding MgO in the finest sizes only, and possibly by screening out some of the finest chromite. Hence a structure is produced made up of relatively large grains of chromite in a matrix largely of forsterite. Grading becomes very important and an excess of free MgO in the matrix can only increase refractoriness. The usual proportioning for chrome–magnesite bricks is between 70/30 and 60/40 chromite–magnesite mixture. There are bricks made with much more magnesite—about 60 per cent—and these are called magnesite–chrome bricks.

Manufacture is by the standard method using dry-press moulding except that sometimes bricks are chemically bonded (e.g. with $MgSO_4$) and fired in the furnace instead of a kiln.

Typical analyses are given in Table 9. The bricks are dark brown and very dense (3·0). Porosity varies from 19 to 26 per cent, the high value giving a rather lighter brick which is an advantage to the designer of, say, a roof. The bricks have low cold crushing strength and are liable to edge and corner damage. Thermal conductivity is rather lower than that of magnesite. Spalling resistance is excellent in most of these bricks but if porosity is reduced by grading or by very high moulding pressures, impairment of spalling resistance may result. Refractoriness is high but R.U.L.

values are rather variable and, at their worst, not very satisfactory. Even the best are deforming at 1600°C maintained temperature.

Slag resistance is excellent to basic slag and iron oxide. A very large amount of FeO can be absorbed by these bricks before refractoriness is impaired, but the brick must expand, and this can lead to another kind of failure, namely by "growth". Carbon deposition can also occur under certain conditions of temperature (450°C) and gas composition (CO high). This is particularly likely if the Fe_2O_3 content of the brick is high. Carbon also causes "growth" and ultimately spalling.

Growth due to FeO is explained as follows, there being two effects. First, the hot face being at about 1600°C, the matrix may melt as low as 1400°C, especially if high in CaO. Liquid is drawn back into the brick pores by capillarity, re-freezing on the the 1400°C isotherm about $1\frac{1}{2}$ in. back. Secondly, FeO is readily absorbed in the spinels (the coarse grains) and as they expand as individual particles so also must the brick. This expansion can be accommodated at the hot porous face, but not at the dense zone along the 1400°C isotherm whither the bond has migrated, and cracking occurs at that zone. Flakes $1\frac{1}{2}$ in. thick fall off. The process then repeats itself. This is called "structural spalling" and similar processes occur in other basic bricks and to a lesser extent in silica bricks (see page 126). It is aggravated by thermal fluctuations.

The main remedy for structural spalling is to keep the CaO content down (1 per cent), particularly in the magnesite fraction. This prevents liquation of the bond. Very low total lime is not easily attained—especially when sea-water magnesite is being used—but to keep it low in the bond should be easier, as only small proportions of specially prepared material would be required.

Magnesite–chrome bricks have very similar properties to chrome–magnesite but are rather less liable to structural spalling. These are the most highly developed basic bricks and they are widely used in the basic open-hearth furnace—in the gas uptakes and burner zones and in the back wall and front wall, and, of course, in the roof of the "all-basic" furnace. Roofs may be suspended, sprung or restrained in compression by downward forces applied from the furnace frame against the thermal expansion of the arch. In suspended roofs special shapes are hung on hangers from supports spanning the furnace roof which can be designed to any shape, including flat. The apparent advantage that damaged bricks can be replaced individually is not always a practical proposition as the hot face tends to become monolithic. These bricks are rather heavy for sprung-arch construction and have rather a high thermal expansion coefficient, which would cause the arch to rise and fall with temperature and the hot face, which would quickly become monolithic, to crack. Recent designs usually incorporate the restrained arch in which the shape of the roof is under some degree of control. The bricks are held on the arc for which their taper was designed and large-scale cracking is less likely to occur but large temperature fluctuations should be avoided and gas kept on even during fettling.

These bricks may also be used in electric steel furnaces and in the hearths of soaking pits and reheating furnaces in which FeO attack is severe. In non-ferrous extraction they find a place in copper reverberatories, particularly in the roof. Magnesite–chrome bricks are mainly used in roofs.

These bricks can be laid dry if well shaped or cemented together in the usual way, or using steel sheet, placed between them, which oxidizes, attacks neighbouring bricks simultaneously, and binds them together. Bricks are also available in metal cases which serve the same purpose. Building is then merely stacking. This technique can be applied with chemically bonded as well as with fired bricks—for example, suspended roofs on open-hearth furnaces have been made with metal-cased chemically bonded magnesite–chrome brick.

16. Carbon

CARBON bricks are made from coke or petroleum coke (which is preferred as it has the higher purity), crushed, size-graded and bonded with tar or pitch. The mixture is moulded or extruded and fired at about 1000°C to make the grade called "carbon" or up to 2500°C in a resistance furnace to produce "graphite". In the former, the tar decomposes to a char which bonds the coke particles together. In the latter the crystal structures of the coke and char develop some of the greater perfection of the graphite lattice and grains grow together to give something like the structure of a polycrystalline metal. These materials are stronger than natural graphite and more readily produced in the shapes and sizes required by industry.

Graphite has higher electrical and thermal conductivities than carbon and is rather denser, but it is not so strong at ordinary temperatures. Properties do depend on manufacturing conditions and on the nature and size grading of the raw material.

These bricks have excellent hot strength and, with a high thermal conductivity, good resistance to thermal spalling. They are scarcely wetted by either metals or slags and are not subject to chemical attack except by oxidizing slags and oxidizing gases, particularly air, CO_2 and H_2O, to which graphite is rather more resistant than carbon. The formation of a protective layer of silicon carbide has been suggested to improve this property. This can be done by heating in an atmosphere of silicon tetrachloride. Carbon will also be attacked to some extent by metals which form stable carbides, including iron. Such attack is not likely to be prolonged but would, of course, contaminate the metal.

One of the most important properties of these materials is their excellent machinability which enables complex shapes to be made.

Both carbon and graphite are used as electrodes in arc furnaces particularly but also in electrolysis plant such as that producing aluminium. Graphite is preferred where a high current density is involved for its lower electrical resistivity, but it is considerably more costly. Carbon is also used as an electrical resistor in resistance furnaces, in the form of rods or tubes or as granules. In this case carbon would be preferred for its higher resistivity.

The main application of carbon bricks or blocks is in iron blast-furnaces. These have been lined entirely with carbon but only in the bosch and hearth does the practice continue to enjoy popularity, and that mainly in the periphery of the hearth. When they are used across the floor of the furnace the high temperature zone is extended very deep toward the foundations because of the high thermal conductivity of the bricks. Molten metal is able to penetrate a long way into the brickwork and causes trouble with large bears, floating hearths and break-outs. These faults have been countered by use of large blocks carefully machined and set dry with extremely accurate joints. Nevertheless, present practice favours the use of carbon only in a ring round the sub-hearth, which is itself made of firebricks, and within the circle of the stave coolers. The high conductivity of the carbon helps these coolers to impose low-temperature isotherms deep into the hearth and so helps to prevent break-outs.

Carbon bricks are established as linings for furnaces making phosphorus, calcium carbide, aluminium and magnesium, and for the conducting hearths of some types of arc furnace.

Plumbago ware is made from fireclay and amorphous (natural) graphite. This is a standard material for crucibles for melting cast iron and other metals. It is not easily wetted and has a high thermal conductivity. It gradually oxidizes so that carbon is lost, and its valuable properties impaired but it is an economical refractory for use under moderately severe conditions.

On smaller scale work graphite has many applications in laboratories and in industry. In powder metallurgy it is used for moulds and plungers for hot pressing. It appears in laboratories as crucibles, as resistors as in the carbon tube or Tamman furnace, and as the heating element or inductor in high-frequency furnaces. It has a wide range of potential uses in rocket engines, in heat transfer systems, and as a moderator in some atomic piles, where very high purity is, however, demanded.

17. Insulating Refractories

All refractories are insulating in some degree, but when it is desirable to minimize the loss of heat without unduly enlarging the structure careful selection from a small group of special materials is desirable.

It is necessary to reduce heat flow by radiation, convection and conduction. The baffling of radiation is simple. A single screen will reduce radiation transfer between two points by at least 50 per cent. Two screens will reduce it by over 67 per cent, three by over 75 per cent, and so on. To reduce convective transfer, the free air space around the hot zone should be divided up into small compartments so that circulation in each is limited. To minimize conduction, the hot zone must be surrounded by a substance of low thermal conductivity at its operating temperature. Gases, except hydrogen and helium, have very low conductivities and air is the obvious choice.

The ideal insulator is, then, some kind of honeycomb structure of minute cell dimensions, filled with air and constructed of something with very low conductivity and extremely thin walls. It should also be rigid at the operating (high side) temperature. Up to about 1500°C porous firebrick is available. It is made from fireclay, mixed with hard wood sawdust or chips. The wood burns out on firing so leaving a light porous brick. High refractoriness can be obtained by careful selection of clay. China clay can be used to give the highest refractoriness. These bricks can be cut with a hacksaw and are very useful for making laboratory furnaces. R.U.L. is always rather disappointing.

The conductivity of insulating firebricks (see Table 11) is not so low as that of kieselguhr, or asbestos bricks, but these are not stable to such high temperatures and would be used beyond insulating firebrick—not above about 900°C. At lower temperatures again glass wool, slag wool, vermiculite, or woolly asbestos can be used, or laminated, crumpled aluminium foil. These materials are packed in blankets which can be assembled outside the normal brickwork.

TABLE 11

Thermal Conductivities of Various Refractories

	c.g.s. units		
	300°C	700°C	1100°C
Silica	0·003	0·004	0·005
Firebrick	0·002	0·002	0·003
Sillimanite	0·003	0·004	0·004
Magnesite	0·011	0·008	0·007
Chrome	0·004	0·004	0·005
Chrome–magnesite	0·005	0·005	0·004
Insulating firebrick	0·0006	0·0008	0·001
Kieselguhr	0·0003	0·0004	—
Asbestos	0·0001	0·0001	—
Slag wool	0·0001	0·0001	—
Carbon	—	0·005	0·008
Graphite	0·21	0·12	0·08
Carborundum	—	0·03	0·02

Very high temperature insulation or radiation baffling is effected in laboratory furnaces, by refractory powders—magnesia, zirconia, or even carbon. The conductivity of the substance in bulk is of little consequence. In all cases it is the porosity or voidage—amount and dimensions—which determines the effectiveness of the insulation, and the greatest difficulty in their use is to maintain the porosity uniform. Very pure material is desirable to reduce the tendency to sinter and so lose porosity. Carbon is, of course, immune from this but could only be used under reducing conditions or in vacuum.

18. Special Refractories

This heading can only cover a miscellany of expensive materials and new processes which have not yet become common.

1. *Electrocast blocks* are made by fusion and casting. Mullite blocks are used in glass tanks. Fused magnesia bricks and mixtures of chromite, bauxite and magnesite fused and cast into spinel bricks are made in U.S.A. and Germany. Porosity is low; R.U.L. is high; spalling resistance is usually poor, but cast magnesite, resistant to thermal shock, has been made. Growth due to FeO absorption is small, because of the very low permeability.

2. *Alumina* can be obtained quite pure from bauxite ore which is a mixture of two hydrates gibbsite $Al_2O_3.3H_2O$ and diaspore $Al_2O_3.H_2O$, usually associated with a large amount of iron oxide from which it is easily separated. Dehydration gives α–Al_2O_3 (corundum) while heating above 900°C forms γ–Al_2O_3. (A β variation can be crystallized out of a sodium carbonate melt.) Fused alumina may be cast to corundum, crushed, ground and graded and formed into laboratory ware, or the prefired γ modification may be used. Ware should be fired at about 1700°C.

Alumina has a melting point of 2015°C which is low compared with that of other special refractories. It can be used up to about 1900°C. The ware may be impermeable to gases if required, but at the expense of some resistance to spalling. Porous ware is less susceptible to thermal shock and should be used where possible. Slag resistance is poor, especially toward FeO and basic slags. Alumina is unaffected by gases, except fluorine, and it stands up well to fused alkalies. The most usual shapes made are tubes and crucibles.

"Alundum" cement is a useful mixture of fused alumina and clay which can be tempered with water and hand-moulded to any shape for laboratory use. It shrinks a little in firing; it is porous and spalls readily, but is cheap and can be used, depending on the grade, up to 1500°–1700°C.

3. *Laboratory alumino-silicates.* Porcelains and mullites can be obtained in tube and crucible form for service up to temperatures ranging from 1200°C to 1650°C. Those for use up to the higher temperatures are usually more sensitive to thermal shock and are usually the most expensive. The same materials are used as insulators, e.g. on thermocouples and electric heating elements, and as electrical insulators for high voltage. Their constitution is similar to that of sillimanite and mullite bricks.

4. *Laboratory silica* is available as "Vitreosil"—a pure silica, fused and drawn out to tube form and worked like glass into crucibles, dishes, and other shapes. Normally this is translucent but it can be obtained clear like glass. This material has a very low coefficient of thermal expansion—almost zero—and very high resistance to thermal shock. It can be used up to 1100°C or 1200°C but usually fails by devitrification, a process hastened by the presence of even small amounts of alkalies, alkaline earths and particularly certain special mineralizers like sodium vanadate and tungstate. Devitrification is to cristobalite so that no damage results until the silica is cooled below 300°C. Continuous use at up to 1350°C or even higher is therefore possible, but failure would always occur during subsequent cooling to room temperature. In industry vitreosil is used for replaceable thermocouple sheaths for use up to steel bath temperatures.

5. *Beryllia* (*BeO*) is used very pure. Its melting point is 2550°C but it sublimes above 2000°C and also reacts with even small amounts of water vapour to form a volatile hydroxide above 1650°C. It is not strong at low temperatures but compares well with other materials over 1500°C. Its thermal shock resistance is particularly good, probably because of its high thermal conductivity.

Beryllia is very unreactive chemically particularly toward metals and carbon and is mainly used for crucibles for containing very pure metals, including alkalies, alkaline earths, rare earths, uranium, silicon—and also nickel and iron. It is useful as a radiation shield in carbon resistance furnaces, having itself a low electrical conductivity, as well as being inert toward carbon. Beryllia dust can be dangerous if inhaled even in small amounts and this can make this useful refractory rather difficult to use.

6. *Magnesia* is made into crucibles for melting pure metals but the manufacture seems to be rather difficult and the product rather less satisfactory than some other pure oxides.

7. *Thoria* (ThO_2) melts at about 3300°C, higher than any other oxide. It is not a very rare material but occurs along with rare earths and its purification renders it rather expensive. Thoria is a basic refractory, reacting with silica but not with basic slags. Its thermal shock resistance is poor. It is radioactive. Its main use is as a crucible for pure metals with which its interactions even at very high temperatures are slight.

8. *Zirconia* (ZrO_2) melts at 2677°C. The oxide is an acid and reacts with basic oxides and slags. It is stable, however, to both oxidizing and reducing atmospheres up to 2200°C (when it reacts with H_2 and N_2) and toward most metals. Pure zirconia occurs in two modifications with an inversion temperature at about 1000°C. Another cubic modification forms and is stable at all temperatures in the presence of lime or magnesia with only a slight fall in refractoriness. The material is prepared either fully stabilized with about 5 per cent CaO or only partially stabilized, with slightly different properties. Neither has very good spalling resistance because if the inversion is fully suppressed the thermal expansion increases. The thermal conductivity is very low, which makes it a good high temperature insulator.

Zirconia is very unreactive toward metals (except titanium) and is particularly useful for containing refractory alloys. It is used as nozzles through which steel flows in continuous casting equipment.

Zirconia is a sufficiently good conductor of electricity at high temperatures that it can be used as the inductor in high frequency furnaces once primed. On the other hand, it is not suitable as a former for a wire-wound resistance furnace.

9. *Zircon* (*$ZrSiO_4$*) melts at 2420°C and is also classed as an acid refractory. It has no inversions but is said to dissociate at 1750°C to zirconia and silica glass. It has a low thermal expansion and hence a good spalling resistance, but this property may be lost if the dissociation is allowed to proceed too far.

Zircon has a variety of rather specialized applications—in the glass industry because of its low reactivity toward acid glasses; in foundries as a moulding sand because of its thermal conductivity; in the remelting of aluminium because of its resistance to wetting by that metal; in boilers where its resistance to attack by oil ash is of value. On the other hand, it is very reactive toward other substances—FeO, fluorspar, and some phosphates—and must be used with care.

10. *Silicon carbide* (*SiC*) *or carborundum* is made by fusing together sand, coke and salt in an electric resistance furnace. Part of the product is silicon carbide which can be crushed and reconstituted as bricks or other shapes, by refiring to sinter, or after bonding with clay. It can be used up to about 2000°C under favourable conditions but it tends to decompose in air, Si burning to SiO_2. If this occurs slowly a glaze forms and protects the rest of the material but it can start burning very violently if the protection breaks down. Spalling resistance is very good. Silicon carbide is very hard and is used as skids in billet heating furnaces. It can be attacked by FeO, however, and cannot be used in this way to very high temperatures. Silicon carbide is also used in tube form in recuperators and in bars or spiral form as electric resistors—globars or silit rods or crusilite rods.

Many of these special refractories serve only very limited markets but at the same time specialized users of such materials are searching continuously for outstanding materials to help them solve their design problems in nuclear technology, aircraft and rockets. The materials sought have to replace and do better than the best metals already available at higher temperatures than they can reach. A review by Livey and Murray[1] has recently surveyed the whole field of possibilities—not only oxides but nitrides, carbides, borides and even sulphides. Few of these are likely to find a place in furnace technology and no more will be said of them here.

The fabrication of articles from these special materials follows the normal pattern outlined for ordinary refractories with a few differences in detail and emphasis. Special refractories are usually made from pure compounds rather than raw ores and the incorporation of fluxes for bonding is not usually possible. Any temporary bonds added must be burned out in firing. Special refractories are often formed by slip casting. Very fine grinding to a few microns is necessary and the particles are dispersed in slightly acid water. Such fine material leads to impermeable ware and assists the sintering process by which the particles are bonded together. This diffusion process proceeds very slowly in the solid state except at very high temperatures so firing is carried out at temperatures much higher than is usual with ordinary bricks. There are, of course, other forming processes such as extrusion of tubes (using a temporary bond), or dry pressing prior to sintering as in powder metallurgy.

Perhaps the outstanding failing of these ceramic materials is that they are all inherently brittle. Their strength in compression is good. In tension strength may be tolerably good, but in bending and particularly under impact, very poor. This has been ascribed to there being many fewer dislocation sources operative during slip (than in metals) so that higher stresses are needed to move them than in the case of metals. If the required shear stress is greater than the yield stress slip is restricted to a small number of slip bands which are often found to be associated with microcracks. When these cracks extend to a critical size they propagate rapidly. Crystals free of such flaws can be bent considerably before breaking. Alternatively, if the number of slip bands is increased (as by bombarding the surface with hard particles before stressing), the ductility can be greatly increased. This explains the brittleness but does not point to any practical way of overcoming it in commercial materials.

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[1] D. T. Livey and P. Murray, Contributing in *Physico-chemical Measurements at High Temperatures*, by J. O'M. Bockris, J. L. White and J. D. Mackenzie.

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This short book list will help the student to find more detailed and specialized treatment than it has been appropriate to include in this volume. (1) is the most comprehensive general textbook on fuels, particularly the revised edition of 1955. (2) deals very fully with coals and coking. A revised edition is in preparation. (3) is the standard work on oil and (4) the standard work on electricity. For the general reader early editions of (4) are probably more useful than the later ones which are perhaps rather too specialized for him. (5) and (6) are essentially reference books. (5) and (7) contain articles which make very valuable up-to-date supplementary reading. (6) is, as the name implies, a data book which has become almost a standard source of facts, figures and formulae. (8) treats refractories from the manufacturer's point of view and is very comprehensive. (9) takes the viewpoint of the user and is probably better suited to the general reader, though applications beyond steelmaking naturally get only brief comment. (10) specializes in basic bricks. It is a vast review of literature on a topic which has not yet been tidied up and it includes many complex equilibrium diagrams as they are applied to basic refractories. (11) is a collection of diagrams with a useful note on how to read them. (12) contains a number of extensive reviews on special refractories and ceramics. Current work in fuel is reported in many places but particularly in the *Journal of the Institute of Fuel*, and in *Fuel*. Current literature is abstracted monthly in *Fuel Abstracts* by the Ministry of Fuel and Power. Current work on refractories appears in the *Transactions of the British and American Ceramic Societies*. The *Monthly Digest of Statistics* (H.M.S.O.) or the *Annual Digest of Statistics of the Ministry of Fuel and Power* are convenient sources of information on economic aspects of fuel.

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